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The Separation of the Hydrogen Isotopes by Electrolysis. Part I

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The equilibrium constants of the reactions $H_2O+2D=D_2O+2H$ and $H_2O+D_2O=2HDO$ are calculated and from these an expression is obtained for the electrolytic separation coefficient, valid when zero-point energy and tunnelling are negligible in the activated state. The change in this coefficient with increase in concentration of the heavy isotope is calculated. Experimental values have been determined for the separation coefficient at different metallic cathodes, ranging from 7.6 to 2.8. Local concentration disturbances round the cathode are not in general important, but may be the cause of the poor separation found with platinum black. The importance of half-quanta in the activated state is discussed. The experimental results considered in the light of the calculations indicate that tunnelling is not very important in the electrolytic separation. The vapor pressures of liquids containing isotopes are considered.

SECTION 1. INTRODUCTION

THE separation of the hydrogen isotopes by electrolysis of solutions of electrolytes in water depends essentially upon the removal of hydrogen from water molecules. The rapidity of the equilibrium reaction $2H_2O=H_3O^+ + OH^-$ compels us to consider the water as the fundamental source of the hydrogen evolved at the cathode.

Reactions at the anode come into question only insofar as the products of the anodic reactions diffuse to the cathode and modify the composition of the solution there. Confining attention to solutions which evolve hydrogen and oxygen in equivalent quantities, the only changes in the nature of the electrolyte during electrolysis are the increase in electrolyte concentration and the change in the relative number of H and D atoms. The effect of local changes in composition round the cathode depends upon the experimental conditions; this point is taken up in Section 3, where it is shown that under the usual conditions of experiment they may for practical purposes be ignored.

The "electrolytic separation coefficient" α is defined by

$$d \log \mathrm{H} = \alpha d \log \mathrm{D}. \qquad (1)$$

When the mol fraction of electrolyte exceeds the atomic fraction of the isotope present in lesser amount, then the nature and concentration of the electrolyte will have some effect upon α. Experiment shows, however, that this effect is not a very large one.

SECTION 2. THEORY OF THE ELECTROLYTIC SEPARATION

In this section it is assumed that the solution surrounding the cathode is in thermodynamic equilibrium with the bulk of the solution (cf. Section 3) and that the mol fractions of all ionic species are small compared with the atomic fractions of both H and D.

The mechanism of the process at the cathode is not always the same in acid and alkaline

solutions. For example, some of the hydrogen obtainable by electrolyzing a KOH solution with a mercury cathode is produced in a secondary reaction between the potassium amalgam and the water; similarly at a lead cathode it is usually supposed that a K-Pb alloy is formed initially, and at cathodes which show no tendency to form alloys with alkali metals, the metallic cation may nevertheless be preferentially discharged if the hydrogen overvoltage is high enough. In solutions of strong acids, direct discharge of hydrogen ions is the only possibility. The various theories of overvoltage proposed have all been designed primarily to explain the empirical relation between current density and overvoltage. The main difference between them concerns the decision as to which of the steps intervening between the original water molecules and the final hydrogen molecules is the slowest step.

We have to consider the consecutive stages:

(a) $$2H_2O = H_3O^+ + OH^-,$$

(b) $$H_3O^+ + M^- = H_2O + H - M,$$

(c) $$2H - M = H_2 + 2M.$$

Stage (b) is the neutralization of a hydrated hydrogen ion by the negatively charged metal M, with formation of a hydrogen atom attached in some way to the surface atom M. Stage (c) represents the desorption of hydrogen in the molecular form from the metal surface.

One theory of overvoltage assumes that (c) is the slow process, (a) and (b) being reversible and in equilibrium. This theory (the essentials of which were originally due to Tafel[1]) has since been modified in various directions, but for the discussion in this section, it is only important that (a) and (b) are assumed to be in equilibrium.

The well-known theories of Erdey-Gruz and Volmer[2] and of Gurney[3] both place the slow reaction at stage (b); they differ fundamentally in that the former associates the slowness with the passage of protons over a potential barrier lying midway across the Helmholtz double layer, and the latter attributes it to the slow penetration of electrons through a potential barrier of a different kind situated between the metal and the ions in the solution.

In the remainder of this paper (Part I) we discuss a number of points which are relevant to any mechanism in which the slow process involved the passage of hydrogen particles over or through the upper part of a potential barrier. We are not here thinking of a mechanism involving the slow leakage of the electrons through the potential barrier connected with the work function.

Corresponding to any special theory of the mechanism of the cathode process there is some definite activated state with which the overvoltage is correlated. Consider first the simplest case, where the activated state consists of entirely free hydrogen atoms. The reaction at the cathode cannot really involve such free atoms because the activation energy would then be prohibitively large, but the calculation forms a basis on which the consideration of mechanisms involving different activated states can be built; this calculation also applies to any activated state which fulfills two conditions: (a) that the total zero point energy in the activated state is zero, (b) that quantum mechanical leakage of the hydrogen particles through the potential barrier is negligible in comparison with the rate at which they pass over the barrier. By combining the result of this calculation with experimental values for the electrolytic separation coefficient we have a new possibility of deducing properties of the activated state.

We make the usual assumption for reaction rates,[4] that the rate of the slow process is the same when the reaction is proceeding irreversibly, in the forward direction only, as the rate in either one direction at equilibrium. This rate is the number of particles in the activated state at equilibrium multiplied by the average velocity with which they travel in the forward direction. Since for our present problem we require only the relative reaction rates of the two isotopes, we first calculate the equilibrium ratio of H to D atoms (and H^+ to D^+ ions) in free space, in equilibrium with water containing H_2O, HDO and D_2O.

[1] Tafel, Zeits. f. physik. Chemie **34**, 200 (1900); **50**, 641 (1905).

[2] Erdey-Gruz and Volmer, Zeits. f. physik. Chemie **A150**, 209 (1930).

[3] Gurney, Proc. Roy. Soc. **A134**, 137 (1932).

[4] Tolman, *Statistical Mechanics*, p. 269 (1926).

Consider the equilibria

$$H_2O+2D=D_2O+2H, \quad (1a)$$

$$H_2O+D_2O=2HDO, \quad (1b)$$

with equilibrium constants in the gas phase K_a and K_b, respectively.

In the equations which follow, and throughout this paper, the subscripts 1, 2, 0, 3, 4 will be used to indicate the following molecular species in order: H_2O, D_2O, HDO, H and D.

We write

$$K_a=F_2F_3^2/F_1F_4^2,$$

where the partition function for H_2O in the gas phase is

$$F_1=\exp\frac{+\zeta_1}{kT}\frac{(2\pi m_1kT)^{\frac{3}{2}}}{h^3}\frac{8\pi^2(8\pi^3A_1B_1C_1)^{\frac{1}{2}}}{2h^3}$$

$$\times(kT)^{\frac{3}{2}}\prod_{i=j_1,\ k_1,\ l_1}\frac{1}{1-\exp(-h\nu_i/kT)}\times 4, \quad (2)$$

where $-\zeta_1$ = energy of H_2O in its lowest state, the zero of energy being the three atoms in their lowest states; m_1 = mass of H_2O molecule; A_1, B_1, C_1, = moments of inertia of H_2O molecule; the ν's with subscripts j_1, k_1, l_1, denote the vibration frequencies of the H_2O molecule; h and k are the Planck and Boltzmann constants.

$$F_3=[(2\pi m_3kT)^{\frac{3}{2}}/h^3]4. \quad (3)$$

The partition functions F_{D_2O} and F_D are similar, except that the statistical weights 4 and 4 become 9 and 6 for D_2O and D, respectively. Since, with the vibration frequencies characteristic of D_2O the quantities $\exp(-h\nu/kt)$ are practically negligible in comparison with unity, even at 100°C, we find for K_a

$$K_a=\exp\left(\frac{+\zeta_2-\zeta_1}{kT}\right)\left(\frac{m_2}{m_1}\right)^{\frac{3}{2}}\left(\frac{m_3}{m_1}\right)^3\left(\frac{A_2B_2C_2}{A_1B_1C_1}\right)^{\frac{1}{2}}, \quad (4)$$

the subscripts having the meanings already given.

For the equilibrium in the gas phase of the three kinds of water molecules we have

$$K_b=F_0^2/F_1F_2. \quad (5)$$

The partition function F_0 is the same as F_1 with the substitution of the appropriate vibration frequencies, and the mass m_0, energy $-\zeta_0$, and moments of inertia A_0, B_0, C_0, of the HDO molecule, except that the symmetry number 2 is omitted and the statistical weight is 6 instead of 4. We then have for K_b

$$K_b=\exp\frac{(+2\zeta_0-\zeta_1-\zeta_2)}{kT}\left(\frac{m_0^2}{m_1m_2}\right)^{\frac{3}{2}}$$

$$\times\frac{A_0B_0C_0}{(A_1B_1C_1A_2B_2C_2)^{\frac{1}{2}}}\times 4. \quad (6)$$

The quantities $-\zeta_1$, $-\zeta_0$ and $-\zeta_2$ enter into Eqs. (4) and (6) as differences, and since the potential function is the same for isotopic molecules,* we have only to consider the differences in the zero-point energies involved, i.e., the half-quanta for the three normal modes of vibration of each molecule. For the molecule H_2O we have taken the values obtained by Mecke[5] and his collaborators in their analysis of the infrared absorption of water vapor.

To obtain the frequencies for the isotopic molecules HDO and D_2O we have made use of the very helpful statement of the problem of the three particle system recently published by Van Vleck and Cross.[6] These authors also carried

* We are here neglecting the change in the force constants in the water molecule caused by the mass difference between H and D. The effect can be estimated on the basis of the Heitler-London theory of binding. For a hydrogen atom the potential energy with respect to the oxygen atom is $E=(1/a_m)f(r/a_m)$ where r is the internuclear distance and a_m is the geometric mean of the quantum mechanical analogues of the Bohr orbits of the valence electrons on hydrogen and oxygen. The same function applies to the binding energy of a heavy hydrogen atom, but the new value of a_m is slightly smaller, since $a=h^2/4\pi^2\mu e^2$ where μ is the reduced mass of the electron in the H or D atom, and a is the (quantum-mechanical) orbit of the atom concerned. Since (a_mE) is the same function of r/a_m for both H and D, the potential energy is a minimum at the same value of r/a_m and $E_{\min}$ is inversely proportional to a_m, whilst $r_{\min}$ is proportional to a_m. Thus from this cause the difference $|\zeta_2-\zeta_1|$ is increased by 30 calories and the nuclear distance of OD as compared with OH is decreased by 0.00027 Angstrom. The latter decrease makes only a negligible difference to the moments of inertia. In the calculation which follows we neglect also the effect of the correction to the energy, which would amount to about 2.5 percent in the value of the separation coefficient.

[5] Mecke, Baumann and Freudenberg, Zeits. f. Physik **81**, 313, 445, 465 (1933).

[6] Van Vleck and Cross, J. Chem. Phys. **1**, 353, 357 (1933).

through a theoretical quantum-mechanical calculation of the potential function of the H_2O molecule, and with the corresponding force constants calculated the three frequencies to be $\omega_\sigma = 3520$, $\omega_\pi = 3560$, $\omega_\delta = 1660$ reciprocal cm (we are here using the subscripts employed by Mecke). The nuclear separation between H and O came out to 1.00 Angstrom, and the valence angle to 100°. Using the same molecular constants, we have repeated the calculation of the frequencies for all three molecules H_2O, HDO and D_2O. The results for HDO are $\omega_\sigma = 3560$, $\omega_\pi = 2600$, $\omega_\delta = 1450$, and for D_2O $\omega_\sigma = 2580$, $\omega_\pi = 2590$, $\omega_\delta = 1250$. As Van Vleck and Cross point out, complete quantitative agreement with experiment is not to be expected in view of the approximations necessary in their quantum-mechanical calculation. We do, however, expect that *the relative values of corresponding frequencies* in H_2O, HDO and D_2O will be fairly accurately given by the calculation, in spite of the differences of 5 and 3 percent, respectively, between the valence angle and the nuclear distance calculated by Van Vleck and Cross, and those found by Mecke, Baumann and Freudenberg. Accordingly we have taken the calculated ratios of ω_σ for H_2O : ω_σ for HDO : ω_σ for D_2O (similarly for the ω_π's and the ω_δ's) and multiplied the frequencies found by Mecke and his collaborators by the appropriate ratios. In this way we arrive at the consistent set of frequencies set out in Table I. These frequencies compare in a very reasonable way with the Raman bands in liquid heavy water observed by R. W. Wood,[7] which are included in Table I in square brackets. The Raman frequencies are naturally all somewhat lower in the liquid than in the vapor.

Mecke and his collaborators show that the moments of inertia of the molecule change slightly with the vibrational level, and in the ground state are not exactly what they would be for a rigid structure, because of the half-quanta of vibration. The difference is small, and we consider that a set of consistent moments of inertia of quite sufficient accuracy for our purpose can be obtained by taking the valence angle of 105° 6′ and the nuclear distance of 0.970 Angstrom found by Mecke for the ground state, and

TABLE I.

	Frequencies in cm^{-1}			Moments of inertia $\times 10^{40}$ A	B	C
H_2O	3795 [3445]	3670	1615	1.027	1.972	2.999
HDO	3838 [3500]	2680 [2623]	1411	1.219	3.142	4.361
D_2O	2782 [2517]	2670	1216	1.846	3.938	5.784

calculating the three moments of inertia for each of the three isotopic water molecules, using H = 1.00777, D = 2.01357, O = 16. For comparison, the values (multiplied by 10^{40}) given by Mecke for the ground state of H_2O are: $A = 0.995$, $B = 1.908$, $C = 2.980$. The axis of least moment of inertia in HDO makes an angle of 20° 38′ with the line joining the H and D nuclei.

With these data Eqs. (4) and (6) give for the equilibrium constants $K_a = 126.9$ at 25° and 49.60 at 100°, $K_b = 3.26$ at 25° and 3.40 at 100°.

With regard to the reliability of these equilibrium constants, we think that since the molecules have practically the same potential function, the case is a very favorable one; the accuracy of the K's turns on the accuracy of the vibration frequencies; our opinion is that the equilibrium constants should be accurate to within ±10 percent.

A knowledge of K_a and K_b enables us to calculate the ratio N_3°/N_4° of free atoms of H and D in equilibrium with water vapor of any isotopic composition. We require, however, an expression for N_3°/N_4° as a function of the (analytical) composition of the liquid water.

For the equilibrium in the liquid phase we have (assuming Henry's law)

$$K_b' = N_0^2/N_1N_2 = [p_1^\circ p_2^\circ/(p_0^\circ)^2]p_0^2/p_1p_2. \quad (8)$$

The p°'s denote vapor pressures of the pure species, and the p's partial vapor pressures. The vapor pressure of pure D_2O is known[8] over the range 20° to 110°. A direct measurement of p_0° is of course impossible because of the rapidity with which the equilibrium (1b) is established through ionization. In Section 4 reasons are

[7] R. W. Wood, Science **79**, 35 (1934).

[8] Lewis and Macdonald, J. A. C. S. **55**, 3057 (1933).

given for the assumption we now make, that the vapor pressure for the pure species HDO is the geometric mean of the vapor pressure of H_2O and D_2O. This makes the quantity in square brackets in (8) equal to unity, and therefore makes $K_b' = K_b$.

The relationships which we now write down are derived simply by combining together the expression for K_a and K_b in (1a) and (1b), the assumption of Henry's law, and the assumption that $K_b' = K_b$. The use of concentrations and pressures instead of activities is evidently allowable with such similar molecules. Writing R_e for the ratio of the (atomic) amounts of H to D in the liquid, and R_g for the corresponding ratio in the vapor:

$$R_g = (2G_1+G_0)/(2G_2+G_0) = (2N_1p_1^\circ+N_0p_0^\circ)/(2N_2p_2^\circ+N_0p_0^\circ). \quad (9)$$

G_1, G_0, and G_2 are the mol fractions of H_2O, HDO, and D_2O in the vapor phase, and the N's are the mol fractions in the liquid.

$$R_g = [\beta(p_0^\circ - p_1^\circ)+p_1^\circ] / [\beta(p_0^\circ - p_2^\circ)+p_2^\circ/R_e], \quad (10a)$$

where

$$\beta = \left\{\frac{-K_b'}{4-K_b'}\,\frac{1+1/R_e}{2}\right\} \pm \left\{\left(\frac{K_b'}{4-K_b'}\,\frac{1+1/R_e}{2}\right)^2 + \frac{K_b'}{4-K_b'}\,\frac{1}{R_e}\right\}^{\frac{1}{2}}, \quad (10b)$$

positive root when $K_b' < 4$, negative root when $K_b' > 4$. When $K_b' = 4$ (as it would be if the two kinds of hydrogen atoms were distributed at random among the oxygen atoms) then

$$\beta = 1/(1+R_e). \quad (10c)$$

For the required ratio of n_3°/n_4° in the gas phase we find

$$\frac{n_3^\circ}{n_4^\circ} = K_a^{\frac{1}{2}} R_g \frac{2+(K_b')^{\frac{1}{2}}A}{2A+(K_b')^{\frac{1}{2}}}, \quad (11a)$$

in which R_g is explicitly given by Eqs. (10a, b, c) and

$$A = [(p_1^\circ(1-\beta))/(p_2^\circ(1/R_e-\beta))]^{\frac{1}{2}}, \quad (11b)$$

where β is given by (10b) or (10c).

Since the ionization potential of D exceeds that of H by 84 calories per gram-atom, the equilibrium ratio of H^+ to D^+ in free space is equal to $n_3^\circ/n_4^\circ \exp(84/RT)$.

We recall that the electrolytic separation coefficient for any process subject to two limitations, namely that the activated state consists of hydrogen atoms or ions without zero-point energy, and that quantum-mechanical leakage through the potential barrier defining the energy of activation is negligible, is given by:

$$\alpha^\circ = d\log \mathrm{H}/d\log \mathrm{D} = (1/R_e)d\mathrm{H}/d\mathrm{D} = (1.414/R_e)n_3^\circ/n_4^\circ. \quad (12)$$

The symbols H and D denote the content (in g atoms) of the isotopes in the liquid undergoing electrolysis, and the superscripts ° indicate the limitations just stated under which α° is given by this expression. The factor 1.414 enters because the relative rates at which particles of H and D pass out of the activated state are inversely as the square root of their masses. The ratio n_3°/n_4° now refers to free atoms or free ions according to which is postulated for the activated state.

Examination of Eq. (11a) shows that in general α° varies with the ratio R_e of H to D. The limiting values of α° in very dilute heavy water on the one hand, and nearly pure heavy water on the other, are

$$1.414K_a^{\frac{1}{2}}(p_1^\circ/p_2^\circ)^{\frac{1}{2}}(K_b'/2) \qquad (\text{As } R_e \to \infty),$$

$$1.414K_a^{\frac{1}{2}}(p_1^\circ/p_2^\circ)^{\frac{1}{2}}(2/K_b') \qquad (\text{As } R_e \to 0).$$

Table II exhibits the dependence of α° upon the isotopic composition of the liquid. The figures taken in order along each row show in outline how α° changes as the proportion of the heavy isotope increases from 0 to 100 percent, for the values of K_b' indicated on the left. The calculation has been made for the activated state consisting of free ions; for free atoms the figures are 14 percent less at 25° and 8.4 percent less at 100°.

It will be noticed that when $K_b' = 4$ the efficiency of the separation is the same over the whole range of composition. Also for electrolysis of water in the neighborhood of 50 percent D, the efficiency is independent of the value of K_b', and has the same numerical value as it has for all compositions when $K_b' = 4$.

TABLE II.

K_b'	%D=	0	10	50	90	100
		Temperature 25°				
2	α°=	13.77	16.23	19.46	25.20	27.52
3.3	α°=	17.68	18.66	19.46	20.99	21.42
4	α°=	19.46	19.46	19.46	19.46	19.46
5	α°=	21.74	20.65	19.46	17.51	17.41
		Temperature 100°				
2	α°=	8.03	9.81	11.07	14.37	15.65
3.3	α°=	10.06	10.61	11.07	12.06	12.17
4	α°=	11.07	11.07	11.07	11.07	11.07
5	α°=	12.37	11.74	11.07	10.01	9.90

The figures set out in Table II have a more general significance than appears at first sight. As they stand, they refer to any separation process in which the activated state consists essentially of free ions (or, subject to the factor exp $(84/RT)$, to free atoms also). In reality, the activated state is never simply this: the hydrogen particles in the activated state are those just at the top of some potential barrier characteristic of the particular slow process which is controlling the reaction rate, and depending for its form and magnitude upon the nature of the cathode surface, and possibly upon the applied cathodic overvoltage. We therefore consider a direct equilibrium between the particles in free space and the particles in the actual activated state, in which they are present at some other relative concentration n_3/n_4 differing from n_3°/n_4°. We write

$$n_3/n_4 = K_c n_3^\circ/n_4^\circ, \qquad (13)$$

where K_c is an equilibrium constant analogous to a distribution coefficient between two phases. To calculate the actual electrolytic separation coefficient α, we have only to multiply α° by the corresponding value of K_c.

The factors determining K_c are discussed in Section 5. The energy of a given particle in the activated state at the cathode surface or in the Helmholtz double layer will not be appreciably affected by the substitution of D for H in the solution. Thus we can look upon α as being the product of two independent factors, one a property of the activated state only, the other a property of the ground state only (i.e., the interior of the solution).

It follows that for all these mechanisms the electrolytic separation coefficient will vary with the composition of the solution quantitatively in the same way.

Our calculation of K_b' gave a value 3.3 at 25°. Reference to Table II shows that this requires that α shall decrease slightly as the composition of the water varies from 0 to 100 percent D; corresponding to the estimated ± 10 percent uncertainty in K_b', we conclude that α should decrease by a fractional amount lying between 10 and 30 percent of its value in very dilute heavy water. This is a theoretical conclusion which has not yet been properly tested by experiment. The available evidence shows that (in the case of electrolysis of dilute alkali hydroxide solutions with nickel cathodes at about 10°) there is not much change in α as the percentage of heavy isotope increases; the data are consistent with the theoretical prediction.

	Atomic percent D	α
Bell and Wolfenden[9]	0.2	4–6
This paper	7	5.2–5.8
Selwood[10]	97	5.5–6.5

The theory of the variation of α with the nature and concentration of electrolyte can be treated in a manner similar to the discussion in this section, but it is much more complex. It is an interesting point that measurements of the electrolyte separation coefficient can be utilized to investigate the thermodynamics properties of certain solutions, at least in principle.

SECTION 3. EXPERIMENTAL

The measurements reported in this section were done with the practical aim of finding the most efficient conditions for concentrating the heavy isotope. An accuracy of about 5 percent in the electrolytic separation coefficient was obtained.

The form of apparatus found most satisfactory is illustrated in Fig. 1. Samples of electrolyte (about 75 cc) are weighed into the electrolysis vessel, and occupy the wider part A; this is cooled (or heated) by surrounding it up to the level B with a suitable bath. The condenser C is needed only when the electrolysis is done above room temperature.

[9] Bell and Wolfenden, Nature **133**, 25 (1934).
[10] Selwood, personal communication.

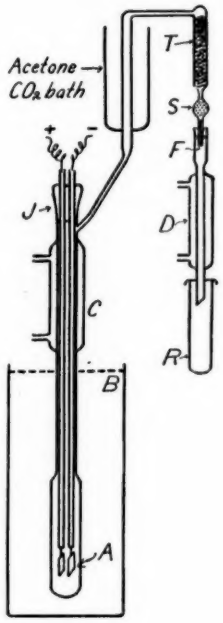

FIG. 1.

About 10 cc of water is electrolyzed and the electrolytic gas burns in a minute flame at the jet F. The water formed is condensed in the small condenser D and collected in a weighed tube R, which is closed with a tin-foil cover.

The electrolytic separation coefficient is calculated from the relationship:

$$\alpha = (\log W_H - \log W_H')/(\log W_D - \log W_D'),$$

where W_H, W_D, and W_H', W_D' are the weights of H and D in the solution before and after a portion of the water has been electrolyzed away.

The ground joint J is not greased but is sealed externally with a thin ring of picein wax. The stream of electrolytic gas passes out of the electrolysis vessel at the temperature of the coldest part of the vessel (about 5° in the majority of the experiments) and loses the water vapor it carries in passing through the vertical trap surrounded by acetone and solid CO_2. The dried gas passes through a spray trap T packed with absorbent cotton, and then through a 10 cc bulb filled with fine sand, to the jet F inside the condenser D. This amount of sand is completely effective in extinguishing the detonation wave which fires back from the jet whenever the gas flow speed is reduced below a critical limit. This simple device has proved completely satisfactory in eliminating all risk of explosion originating at the jet. The jets are made simply by partially fusing the end of a piece of thick-walled Pyrex

TABLE III.

Cathode	Apparent current density	Electrolyte	Atomic % of D	α
Pb	1 (a)	KOH ½N	7	7.4
Pb	1 (a)	" "	8	7.2
Pb	1.3 (s)	H_2SO_4 "	8	6.2
Pb	1.3 (s)	" "	9	6.6
Pb	1.5 (b)	" "	12	6.3
Pt	1 (s)	KOH "	7	7.6
Pt	1 (s)	" "	8	6.5
Pt	1 (s)	H_2SO_4 "	8	5.7
Pt	1 (s)	" "	9	5.7
Pt	14 (b)	" "	8	5.7
Pt	14 (b)	" ¾N	12	6.4
Pt	14 (b)	" 1N	18	6.3
Pt (black)	2	" ½N	12	4.6
Pt (black)	2	" ¾N	15	4.7
Pt (black)	2	" 1N	21	4.7
Pt (activated)	4	" ½N	7	4.7
Pt (activated)	4	" ¾N	9	4.7
Pt (activated)	32	" ½N	8	3.4
Pt (activated)	32	" 1N	11	3.6
W	6 (b)	" ½N	12	5.3
Fe	1 (s)	KOH ½N	7	7.6
Fe	1 (s)	" "	8	6.9
Ni	1 (s)	" "	7	5.5
Cu	1 (s)	KOH ½N	7	6.8
Cu	1 (s)	H_2SO_4 ½N	7	5.5
Cu	1 (s)	" ¾N	8	5.8
Ag	1 (s)	KOH ½N	7	5.3
Ag	1 (s)	" "	8	5.8
Ag (c)	1 (s)	H_2SO_4 "	8	6.0
Ag (c)	1 (s)	" "	10	5.6
Hg	0.7	" "	8	2.8
Hg	0.7	" "	9	2.9
Hg	0.7	" ¾N	10	2.7
Hg	0.7	" 1N	15	2.8
Ga (supercooled)	1.5	" ½N	8	4.1
Ga (supercooled)	1.5	" "	10	4.6

(a) metal disintegrates; (b) smooth surface; (s) surface roughened with sandpaper; (c) metal blackened during use.

capillary so that the diameter of the orifice is about 1/15 mm.

The condensed water is always slightly acid with nitrogen oxides formed at the outer surface of the flame. The water produced was weighed, then made alkaline with a few mg of anhydrous sodium carbonate, and a few crystals of potassium permanganate added. The solution is boiled for a short time to free it from CO_2 and then distilled, avoiding bubble-formation as far as possible. The specific gravity was determined in a 6 cc pycnometer to an accuracy of 2 parts in a hundred thousand. The composition of the water was calculated on the basis of the figure 1.1056 for pure D_2O (d_{25}^{25}) assuming a linear relationship between composition and specific gravity.

In making up the electrolyte solutions the heavy water mixture was twice distilled from slightly alkaline permanganate before use. Ordinary C.P. potassium hydroxide and sulphuric acid were used, the acid having first been subjected to electrolysis for some time to remove metallic impurities.

In some of the experiments the water vapor was not frozen out of the gas stream; in these cases the whole of the vapor carried by the gas is of course condensed out along with the water formed in the flame, since the system operates at constant volume, being in fact normally closed by a drop of water hanging at the exit of the tube from the condenser D. A correction is therefore very easily applied to take account of this source of slight error.

The experimental results are recorded in a condensed form in Table III. The temperature of the electrolyte was between 10° and 26° in all cases, and it is sufficiently close to compare the results on the supposition that the temperature was in the neighborhood of 20°.

The second column gives the apparent current density in amperes per sq. cm when no allowance is made for the actual condition of the surface. Some idea of the relative current densities is obtained by taking into account the notes referred to by letters in brackets following the figures. The composition of the solution with respect to electrolyte is given in the third column, and with respect to the isotopic content in the fourth. These are average values during the electrolysis of the 10 cc samples. The last column gives the values of the electrolytic separation coefficient α.

The main conclusion is that there are very considerable differences between different metals, the order of efficiency taking a general view of the figures both for acid and alkaline solutions being: Pt and Pb; Fe; Cu and Ag; Ni; W; liquid Ga; Hg. Platinum black and "activated" platinum are omitted from this series for the reason discussed below.

The results for bright platinum show that the current density can be varied considerably without much affecting the efficiency. This has also been commented on in the case of nickel cathodes and alkali hydroxide solutions by Urey,[11] and by Bell and Wolfenden.[9]

The results for mercury and for bright platinum show that the electrolyte concentration and the proportion of heavy isotope can be doubled without noticeable effect on the efficiency. In general the value of α is about 15 to 20 percent lower for the same metal in the acid than in the alkaline solution; silver is only an apparent exception, since during the electrolysis in sulphuric acid the metal is blackened, presumably because of slight cathodic reduction to sulphide, so that the surface of the cathode is no longer simply silver.

The "platinum black" electrodes were prepared in the usual way by deposition from a platinic chloride solution, without addition of any lead acetate. The electrodes referred to as "activated" were also platinum electrodes covered by a grey-black deposit of platinum, but the activation of the surface was the result of electrolyzing for some time with alternating current of 60 cycles.

Electrolysis of water by 60 cycle alternating current has been studied by Shipley and Goodeve,[12] who found that a large proportion of the electrical energy could be used to effect gas evolution. Our experience was, that although this is so for a short time, the electrodes soon became so strongly activated that the yield of gas fell to practically nothing. This applies both

[11] H. C. Urey, Science **78**, 566 (1933).

[12] Shipley and Goodeve, Trans. Am. Electrochem. Soc. **52**, 375 (1927).

to platinum and to silver electrodes; the latter, as Shipley and Goodeve found, are not seriously corroded; nevertheless silver becomes in time extremely active in causing the recombination of the electrolysis products.

The local concentration of heavy water at the cathode

During electrolysis the liquid round the cathode tends to increase in content of D relative to the main bulk of the solution, since the mobilities of the different kinds of hydrogen ion are not very different,[13] but the light isotope is preferentially discharged. This tendency is offset in several ways: by stirring of the solution by the gas evolved, by convection caused by temperature inequality, and by diffusion. With current densities such as are used in practice there is certainly vigorous stirring of the bulk of the liquid by the stream of bubbles leaving the electrodes. It may be, however, that whilst discharge of ions takes place all over the surface, the actual growth and detachment of bubbles tends to occur mainly at certain favored places, the hydrogen atoms or molecules moving over the metal surface to these places. In that case there would be a very thin layer of liquid covering parts of the cathode surface relatively remote from the places of bubble formation, which would not be effectively stirred. In such a stagnant layer mixing would take place mainly by convection and diffusion. As regards convection, there is a liberation of about one-tenth of a calorie per second per volt overvoltage for a current density of 1 ampere per sq. cm, but the greater part of this will be taken up by the metal in the first place.

As regards diffusion, an estimate of the effect to be expected can be made in the following way: we assume that covering the greater part of the cathode surface there is a thin layer of liquid which does not suffer mixing into the main bulk of the solution either by mechanical means or by thermal convection. Outside this layer there is complete mixing by the stream of bubbles.

A stationary state will then be set up in which a definite composition is maintained at the boundary of the layer, and a definite diffusion gradient is established across the layer. The conditions for such a stationary state *in a solution of an acid* are that the *whole of the current across the boundary must be carried by hydrogen ions*, and that the rate of neutralization of ions of each isotope is equal to the rate of migration of the isotope into the layer minus the rate of diffusion of the isotope out of the layer.

It is sufficient to consider the special case of a dilute solution of a strong acid, in water containing a small proportion of D.

Let C_H, C_D, and C_H', C_D' define the isotopic composition of the liquid, expressed in g atoms of H and D per cc in the bulk of the solution, and at the surface of the metal, respectively. Practically the whole of the D isotope is in the form of HDO molecules, and we assume for the purpose of obtaining a rough estimate, that the relative numbers of H and D ions at any place are in the ratio of the total H and D concentrations at that place. We neglect the transport of water arising from hydration of the ions. For the stationary state we have

$$\frac{K}{x_0}(C_D - C_D') \approx \frac{I}{F}\left(\frac{C_D'}{C_D' + \alpha C_D'} - \frac{C_D}{C_D + C_H}\right), \quad (14)$$

where K = diffusion coefficient of HDO in H_2O, in cm^2 $sec.^{-1}$; I = current density in amperes per sq. cm; F = the Faraday, α = the electrolytic separation coefficient; x_0 = thickness of stagnant layer, in cm. It is reasonable to ignore the effect of the difference between C_D' and C_D provided this difference does not amount to more than say 2 percent. We use Eq. (14) to estimate in a typical case what thickness x_0 of the unstirred layer would be required to produce a 2 percent excess of C_D' over C_D. We take:

$$C_D/(C_D + C_H) = 0.05; \quad C_D'/C_D = 1.02; \quad I = 1;$$

$$\alpha = 7; \quad K = 2.5 \times 10^{-5}.$$

This gives $x_0 \approx 4 \times 10^{-3}$ cm. It is not obvious than an unstirred layer of this thickness may not cover part of the surface, and it is therefore possible that the experimental values of α are a little lower through this cause than the correct value, which would be found at much lower current densities.

[13] Lewis and Doody, J. A. C. S. **55**, 3504 (1933).

According to Eq. (14) the value of x_0 remains of the same order of magnitude as α increases from about 2 to infinity.

The experimental results, indicate that the effect of local concentration round the cathode is small: thus when the current density at a smooth platinum electrode is increased 14-fold, there is no decrease in α whereas Eq. (14) indicates a decrease depending upon the value of x_0. We conclude that with smooth metal cathodes the effect of any local increase in concentration in heavy water can be neglected in determinations of α which on other grounds do not claim an accuracy greater than about 5 percent.

When the cathode surface possesses a very irregular structure, as for example when a metal is coated with platinum black, the situation is different. The tendency will be for ions to be discharged at the outer points, but insofar as any electrolysis takes place within the irregular shaped cavities, stirring, convection and diffusion will all be much less effective. This would account for the low efficiency of the separation on platinized platinum cathodes, and the explanation is supported by the fact that increase of current density in this case did lower the efficiency still further.

Section 4. The Vapor Pressure of Liquids Containing Isotopic Molecules

In Section 2 the assumption was made that the vapor pressure of pure HDO ($p_0°$) would be the geometric mean of the vapor pressures of H_2O ($p_1°$) and D_2O ($p_2°$). It happens that in this particular case examination of the numerical magnitudes involved shows that so far as the requirements of the argument in Section 2 are concerned, the situation is much the same if one merely assumes that $p_0°$ lies somewhere near the mean of $p_1°$ and $p_2°$, because in the range 20° to 110° $p_2°/p_1°$ is of the order 0.9.

It is, however, desirable to discuss the relative vapor pressures of liquids that differ only in having different isotopic atoms in their molecules. We formulate the discussion in terms of the particular example water, applying the conclusions reached to the question of the vapor pressure of the species HDO.

The partition function for an isolated H_2O molecule in the gas phase is

$$f_1=\exp\frac{-\chi_1}{k\nu}\frac{(2\pi m_1 kT)^{\frac{3}{2}}}{h^3}V_1\prod_{i=j_1,\,k_1,\,l_1}\frac{1}{1-\exp(-h\nu_i/kT)}\frac{8\pi^2(8\pi^3A_1B_1C_1)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{2h^3}\cdot 4, \qquad (15)$$

where χ_1 = the energy in its lowest state of an H_2O molecule, the zero of energy being the same molecule in its lowest state in the liquid. V_1 = the accessible volume per molecule in the gas phase.

The other symbols have the meanings defined for Eq. (2). Ideally we should solve the mechanical problem for the whole mass of water and use the normal modes of quasi-oscillation and with these the appropriate expressions $1/1-\exp(-h\nu_i/kT)$ to replace the translational part of (15). Instead of the complete treatment, which is not possible, we write for the partition function of a molecule in liquid water:

$$g_1=\prod_{i=m_1,\,n_1,\,o_1}\frac{1}{1-\exp(-h\nu_i/kT)}\prod_{i=r_1,\,s_1,\,t_1}\frac{1}{1-\exp(-h\nu_i/kT)}\frac{8\pi^2(8\pi^3A_1'B_1'C_1')^{\frac{1}{2}}}{2h^3}(kT)^{\frac{3}{2}}\cdot 4, \qquad (16)$$

where the ν's with the subscripts m_1, n_1, o_1, denote the internal vibration frequencies of the H_2O molecule in liquid water, and the subscripts r_1, s_1, t_1, denote the three frequencies of quasi-oscillation of the molecule as a whole.

A_1', B_1', C_1' are the moments of inertia of the H_2O molecule in the liquid.

In g_1 the three frequencies with the subscripts r_1, s_1, t_1 are identified as the quasi-oscillatory motion of a simple molecule in the potential field of the surrounding molecules, but they can be thought of as averaged values of the quasi-frequencies in a large aggregate of liquid molecules. The condition that the vapor shall be

saturated is $f_1 = g_1$. Assuming that the saturated vapor has the molar volume of a perfect gas, we can write $V_1 = kT/p_1^\circ$ and obtain at once an expression for the vapor pressure of the liquid. Similar expressions can be written for the vapor pressures p_0° and p_2° of liquid HDO and D_2O, replacing the subscripts 1 by 0 or by 2 wherever it occurs in the partition functions.

Water vapor is a very imperfect gas, so that we ought in the vapor pressure equation to take account of interactions between gas molecules as well as between molecules in the liquid. The use of a harmonic oscillator and Planck functions for intermolecular motion in the partition function of a liquid is also a very approximate procedure, but our conclusion which depends on the differences between molecules containing isotopes would not be invalidated by modifications in these details.

A liquid is a system intermediate between a gas and a solid, and a range of possible simplified mechanical models can be imagined which approach more or less closely one of two extremes. In the case of water we utilize the measurements recently made by Lewis and Macdonald[14] of the vapor pressure of pure D_2O to obtain at least a clear indication of the proper choice of idealized mechanical model from which to calculate the vapor pressure of pure HDO.

The experimental data are reproduced by the equation

$$p_2^\circ/p_1^\circ = 1.35 \exp(-259/RT) \qquad (17)$$

in the range 20° to 90°. The fact that the latent heat of evaporation is larger for the heavier molecule, in spite of the intermolecular forces being the same, is in part to be attributed to the lower zero-point energy of the quasi-oscillations of the heavier molecule. The generalization that as between chemically similar substances the one of higher molecular weight usually vaporizes at higher temperatures is a manifestation of the part played by the zero-point energy in the latent heat of vaporization.[15]

We consider first the interpretation of the factor 1.35 in Eq. (17), and for this purpose we can compare the figure 1.35 with the different numerical factors obtained by making different extreme assumptions as to the molecular mechanics of the liquid.

Case I

The molecules rotate freely in the liquid as in the gas, and have the same moments of inertia. The frequencies of the quasi-oscillation (as well as the internal frequencies) are such that $h\nu > kT$. Then from the partition functions (15) and (16) we obtain for the ratio of the vapor pressures of D_2O and H_2O

$$p_2^\circ/p_1^\circ = (m_2/m_1)^{\frac{3}{2}} \exp((-\chi_2+\chi_1)/kT) = 1.17 \exp((-\chi_2+\chi_1)/kT). \qquad (18)$$

Case II

This differs from Case I only in the assumption that for the quasi-oscillation frequencies we have the relationship $h\nu \ll kT$; whence

$$\frac{1}{1-\exp(-h\nu/kT)} \approx \frac{kT}{h\nu} = \frac{2\pi kTm^{\frac{1}{2}}}{hK^{\frac{1}{2}}}$$

where m is the mass and K the force constant of the quasi-oscillator considered. The assumption of so low a frequency is of course physically equivalent to assuming practically free translation. This leads to

$$p_2^\circ/p_1^\circ = \exp(-\chi_2+\chi_1)/kT. \qquad (19)$$

Case III

Here we assume that the rotational degrees of freedom in the gas are in the liquid replaced by oscillation for which $h\nu > kT$, and that there are no lateral quasi-oscillations of type assumed in Case I. This gives us

$$\frac{p_2^\circ}{p_1^\circ} = \left(\frac{A_2B_2C_2}{A_1B_1C_1}\right)^{\frac{1}{2}} \exp\frac{(-\chi_2+\chi_1)}{kT} = 2.63 \exp\frac{(-\chi_2+\chi_1)}{kT}. \qquad (20)$$

Case IV

Finally we have the extreme case which is the opposite of Case II: both the rotation and the translation of the gas molecules are replaced in

[14] Lewis and Macdonald, J. A. C. S. **55**, 3057 (1933).

[15] Cf. Urey, Brickwedde and Murphy, Phys. Rev. **40**, 1 (1932).

the liquid by oscillation for which $h\nu > kT$. Then

$$\frac{p_2^\circ}{p_1^\circ} = \left(\frac{m_2}{m_1}\right)^{\frac{3}{2}} \left(\frac{A_2B_2C_2}{A_1B_1C_1}\right)^{\frac{1}{2}} \exp \frac{(-\chi_1+\chi_1)}{kT}$$
$$= 1.17 \times 2.63 \exp (-\chi_2+\chi_1). \quad (21)$$

In the present instance of water, we attribute the excess of 259 calories in the latent heat of vaporization of D_2O as compared with H_2O to the net result of the operation in opposite directions of two effects: the zero-point energy differences of the quasi-oscillation of the H_2O and D_2O molecules as a whole, and the difference between these molecules in respect to the decrease in the internal vibrational zero-point energies associated with the fact that the Raman frequencies in the liquid water[7] are lower than in the vapor; the effect of the former outweighs the latter, so that the zero-point energies of the quasi-oscillators must be considerably greater than 259 calories. Case II is therefore ruled out.

Comparing the empirical constant 1.35 with Case I, III and IV we conclude that the actual condition of liquid water approximates more closely to Case I, i.e., there is nearly free rotation of the water molecules.

Returning now to the vapor pressure of the species HDO we remark that Cases I, III and IV all predict for HDO a numerical factor multiplying the exponential term in the expression for the vapor pressure ratio p_0°/p_1° which is less than 4 percent different from the geometric mean of the corresponding factors for D_2O and for H_2O (unity for the latter).

Further, if we consider the fact that the quasi-oscillation frequencies depend on numbers as close as the reciproçal square roots of 18, 19 and 20, and if we examine the differences between the Raman frequencies and the infrared absorption frequencies given in Table II, we see that the latent heat of evaporation of HDO would not be far from the arithmetic mean of the other two. The arithmetic mean appears as an exponent and corresponds again to the geometric mean relationship for the vapor pressure of HDO. We conclude that for the different kinds of water, the geometric mean relationship cannot be a bad assumption.

From the data of Taylor and Jungers[16] it appears that the vapor pressure of liquid ND_3 is related to NH_3 by the expression: $p_{ND_3}/p_{NH_3} = 1.315e^{-191/RT}$. The moments of inertia[17] of NH_3 are 2.79, 2.79, 4.37 and of ND_3 5.31, 5.31, 8.74. Reasoning as above, we have for comparison with the experimental factor of 1.315, in Case I 1.275, in Case III 2.69. Thus the molecules rotate nearly but not quite as completely in the liquid as in the vapor.

Just after the completion of this paper, Lewis and Schutz[18] report that the vapor pressure of deutacetic acid CH_3COOD is not lower but higher than that of ordinary acetic acid. It seems to us that the mechanical condition of acetic acid may well approach more closely to Case IV than to Case I, since the rotation of the double and single molecules in the vapor phase may be considerably hindered in the liquid phase by association to larger aggregates, and we note that if water showed the behavior corresponding to Case IV the vapor pressure of D_2O would be 2.2 atmospheres at the boiling point of H_2O. The mass difference between heavy and light acetic acid is relatively much less than with water or ammonia, so that the half-quanta of the quasi-oscillations are less important in the liquid acetic acids. Of course the moments of inertia also differ relatively less with the acetic acids but the half-quanta unlike the moments of inertia enter into the partition functions exponentially. The problem offered by a largely associated vapor is naturally more complex than when the association can be neglected.

Section 5. The Activated State for Electrolysis

In Part II of this paper we discuss the details of three mechanisms which have been proposed for the process occurring at the cathode during the electrolysis of water, in the light of the available data on the isotopic separation, and from the standpoint of the theory of hydrogen overvoltage. In this section we confine our discussion to the reason why the values of the separation coefficient on different metals are as low as experiment shows them to be.

The highest electrolytic separation coefficient so far found is only a little over one-third of the

[16] Taylor and Jungers, J. A. C. S. **55**, 5057 (1933).

[17] W. S. Benedict, personal communication.

[18] Lewis and Schutz, J. A. C. S. **56**, 493 (1934).

maximum value of approximately 19 calculated on the assumption that penetration through the barrier is negligible. This is to be expected. The activated state whatever its nature is not at a very much higher level than the initial state. One sees this from the fact that the temperature coefficient of the rate of electrolysis at different cathode potentials corresponds to an activation energy of about 18,000 calories for zero overvoltage at a mercury cathode, and decreases as the overvoltage is raised. Thus the activated state must be one in which the hydrogen particles are still strongly bound to other atoms. For example, if the activation is required for the passage of an H or D ion from its hydrated state to a state in which it is bound to the metal, then at the summit of the barrier it is to some extent bound to both oxygen and metal. Or, if the slow process were the desorption of hydrogen molecules the activated state would be one in which the hydrogen atom is bound both to another hydrogen atom and to the metal.

In any such activated state the particle at the summit of the barrier is momentarily not changing its potential energy as it moves forward over the barrier, and for this motion along the path no half-quantum is to be considered (instead we have tunnelling, which in practice is treated as a separate problem). Motion in a plane normal to the classical path of the particle will be accompanied by increased potential energy, and may be thought of as giving rise to two half-quanta. If the particle at the summit of the barrier is partially bound to several metal atoms in the surface of the cathode, additional degrees of freedom with associated half-quanta will enter.

Thus the constant K_e introduced at the end of Section 2 depends on the relative sizes of these half-quanta in the activated state for the two isotopes. The larger the half-quanta the smaller will be the ratio n_3/n_4 in the activated state compared with n_3/n_4 in free space, which means a low value for both K_e and the electrolytic separation coefficient. In general terms one would naturally assume that in respect of these half-quanta the activated state is intermediate between the initial state of a hydrogen particle in water and the state of a free hydrogen particle with no half-quanta; so that the value of α must lie between 1.4 and 19. The experimentally found range of values seems entirely reasonable from this point of view. There will naturally be differences from one metal to another, but the order in the series of separation coefficients is not related in any obvious way to any one property of the metals.

We remark here that the importance of taking account of the existence of half-quanta in the activated state is quite general for the relative rates of reactions involving isotopes: consider a bimolecular reaction such as $H_2+I_2=2HI$ where in the activated state there are six half-quanta to consider. It is conceivable that for certain reactions of this type, just as has been pointed out by Polanyi[19] for the particular case when the initial state involves free atoms, that the heavier isotope will react more rapidly. The general condition for this to happen is simply that the sum of all the half-quanta of vibration in the activated state exceed this sum for the initial state by a sufficient amount to outweigh the velocity factor 1.414 and any tunnelling which may take place. It is to be expected that examples of all intermediate cases will be found.

As long ago as 1919 Lindemann[20] drew attention to the fact that in principle isotopes could be separated by means of chemical equilibria. Exact calculations of several gaseous equilibria involving heavy hydrogen have been given by Urey and Rittenberg[21] who show also that the differences in the (equilibrium) electrode potentials of the heavy and light isotopes are too small to produce any appreciable separation by fractional electrolysis. The advantage (for the separation) of using reaction rates rather than an equilibrium process arises entirely from the possibility of selecting a reaction for which the activated state has a lower zero-point energy than the final state (or of finding a reaction in which there is a potential barrier which allows some tunnelling). For a favorable reaction the lighter isotope is most plentiful in the first material formed, no matter in which direction the reaction proceeds. This is in marked contrast to equilibrium processes.

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[19] Polanyi, Nature **133**, 26 (1934).
[20] F. A. Lindemann, Phil. Mag. [6] **33**, 173 (1919).
[21] Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933).

In a preliminary note[22] on the experimental results, we expressed the view that if the activation is required to loosen the binding of an H^+ or D^+ ion to water, and that the potential barrier representing this activation lies symmetrically in the Helmholtz double layer, then the well-known results of Bowden[23] indicate that this barrier is 1.5 Angstroms in total width; the height of about 18,000 calories may be in effect diminished by the fall of potential across the double layer to something like 5000 calories for the high current densities employed in practice. On metals of low overvoltage the barrier is still lower. If one assumes that the symmetrical barrier is roughly parabolic in form, then the penetration of the barrier occurs near the top and can be calculated by a formula due to Wigner[24] which expresses the total amount of non-classical penetration of the barrier in terms of the curvature at the top of the barrier. For a barrier which is approximately an inverted parabola with a curvature at the top equal to that of a parabola of height 5000 calories and half-width at the base of 0.75 Angstrom it appears that the effect of the leakage would be to increase the rate of discharge of H by about 20 percent and of D by about 10 percent, which is only of secondary importance as a contribution to the separation.

In a personal communication Messrs. Ogden and Bawn of the Manchester laboratory inform us of the results they obtain by using Eckart's exact solution[25] of the Schrödinger equation. They find a very much greater leakage. This is directly traceable to the form of Eckart's potential, which has a very much greater curvature near the top than the surface we have considered. This strong separation of the isotopes is not found in practice, and it seems to us that the Eckart barrier has altogether too sharp a curvature at the top to correspond to the actual conditions. But in any case the interpretation of so small a width for the Helmholtz double layer is very difficult; if the barrier is in reality wider the curvature and hence also the contribution to isotope separation made by quantum-mechanical leakage may be even less than in our original assumption.

[22] Topley and Eyring, J. A. C. S. **55**, 5058 (1933).
[23] Bowden, Proc. Roy. Soc. **A126**, 107 (1929).
[24] E. Wigner, Zeits. f. physik. Chemie **B19**, 203 (1932).
[25] C. Eckart, Phys. Rev. **35**, 1303 (1930).

An X-Ray Study of the *n*-Aliphatic Alcohols, $C_{10}H_{21}OH$ to $C_{18}H_{37}OH$*

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An x-ray study of the series of *n*-aliphatic alcohols $C_{10}H_{21}OH$ to $C_{18}H_{37}OH$ has been made. Spacings along identity periods perpendicular to the 001 planes (*c* spacings) have been measured at room temperature and at −50°C. By plotting these *c* spacings against the number of carbon atoms in the chain, it is shown that there are two distinct crystalline modifications, the second appearing only in those members having even numbers of carbon atoms. The common (α) modification is shown to crystallize with the *c* axis approximately at right angles with the 001 plane while the other (β) has the *c* axis at an angle of approximately 51° 55′ with the 001 plane. The packing at the ends of the molecules is different in these two modifications. A spectrograph to make such x-ray studies at low temperatures has been designed and constructed. These studies are the foundation of a calculation of the intensities of such *c* spacing reflections presented in a following paper.

INTRODUCTION

SERIES of organic compounds, particularly long chain aliphatic compounds, have always yielded results of great interest when studied by x-ray methods.[1] Such series as have been studied in this manner are the straight-chain hydrocarbons, the *n*-aliphatic acids and the saturated aliphatic ketones. Other long chain aliphatic compounds have been studied, for example, unsaturated acids, dicarboxylic acids, esters and soaps, but in these cases, the series have never included more than two or three individual members. The accuracy of this previous work, as regards the spacing along the *c* axis, is open to serious criticism. From the experimental results of Slagle and Ott,[2] it is known that the observed *c* spacings do not necessarily give the projection of the chain length or double the chain length, as the case may be, of that particular chain present in greatest quantity in the sample but that the observed spacing corresponds to an "average" length of all the various chain lengths present. Consequently, the presence of neighboring members in a sample of a supposedly pure compound would tend to make the observed value inaccurate as regards the true *c* spacing for that compound. This is undoubtedly the case with some of the values of *c* spacings reported in previous work and accounts for some of the anomalies which have been observed.

In this laboratory, the series of *n*-aliphatic alcohols, $C_{10}H_{21}OH$ to $C_{18}H_{37}OH$, of high purity, were placed at our disposal through the courtesy of Professor Reid.

The *n*-aliphatic alcohols have been studied to some extent by Malkin.[3] With a Muller spectrograph and iron $K\alpha$ radiation, the *c* spacings were observed for the *n*-alcohols C_{12}, C_{14}, C_{16}, C_{18}, C_{19}, C_{21}, C_{22}, C_{24} and C_{25} by measuring the reflections from melted and pressed samples on glass plates. It is believed that the present study of the alcohols is justified, because of the high purity of the materials as well as the fact that the available series, although shorter than that at the disposal of Malkin is complete in every member while the other shows many absences of individual compounds.

In connection with the results of Slagle and Ott, mentioned above, concerning known simple and complex mixtures of fatty acids, a similar study of complex mixtures of these alcohols should prove to be of some interest.

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† Pennsylvania state fellow under the National Fellowship Plan; holder of the John Wiley and Sons' fellowship.

[1] Compare Strukturbericht, Leipsig (1931) and S. B. Hendricks, Chem. Rev. **7**, 431 (1930).

[2] Slagle and Ott, J. A. C. S. **55**, 4396, 4404 (1933).

[3] Malkin, J. A. C. S. **52**, 3739 (1930).

Experimental

The alcohols used in this work were prepared by J. D. Meyer,[4] working under the direction of Professor E. E. Reid and are of a high degree of purity. The melting points were determined with good precision from a time-temperature cooling curve, according to the method introduced by Andrews, Kohman and Johnston.[5] These "setting point" values are indicative of the purity and are to be found in the work mentioned above.

The source of x-rays used throughout the course of this work was a metal hot filament type x-ray tube with aluminum windows made in the Seemann Laboratories in Freiburg i. Br. A copper anticathode was used and when operated at *ca.* thirty kilovolts and twenty to thirty milliamperes the radiation consisted essentially of copper $K\alpha$ radiation. A nickel filter removed the copper $K\beta$ radiation as well as some of the continuous region. At no time during the course of the spectrographic work was any radiation other than copper $K\alpha$ observed; in particular, the L series of tungsten was absent.

The two spectrographs used were both of the Bragg oscillating crystal type. The material to be studied was placed on a glass plate either by melting, crystallizing from a solvent or pressing the solid crystals. This prepared plate was then mounted upon the crystal table of the spectrograph and the x-ray reflections were recorded photographically. Reflection occurs according to the Bragg formula, $n\lambda = 2d \sin \theta$. According to the usual method, when the crystal plate has been oscillated so that sufficient length of exposure has been afforded the reflections on one side of the primary beam, the crystal table is rotated 180° and the procedure repeated on the other side. Thus, by measuring the distance between corresponding lines on either side of the primary beam, the glancing angle θ can be ascertained, knowing the essential dimensions of the spectrograph. Knowing θ, $\sin \theta$ can be found and since n the order of reflection (obtained definitely by observation of several orders) and λ the wave-length of copper $K\alpha$ radiation are known, the Bragg formula can be solved for d, the interplanar distance. The value used for the wave-length of copper $K\alpha$ radiation is 1.538674A as obtained from Siegbahn[6] and is the value of the center of gravity of copper $K\alpha_1$ and $K\alpha_2$. The opening of the slit was 0.1 mm throughout the entire work in both spectrographs.

The value of the interplanar distance measured in this manner, when applied to crystal analysis, is not to be confused with the spacing along the c axis of the crystal. It is rather the projection of the spacing along the c axis on a line perpendicular to the glass plate. For this reason, a graphical comparison of these "projection" spacings can be used to show the presence of various modifications when these modifications make characteristic angles with the glass plate. For the purposes of brevity and to follow the usual custom, the projection of the c axis will be referred to merely as the c axis and the observed spacings will be listed as c spacings.

Since the materials used have a melting point range of from 57°C to 5.9°C, it was necessary[7] to design and construct a spectrograph which would keep the sample cooled sufficiently for the material to remain solid. However, the majority of the x-ray diagrams of the alcohols which melt above room temperatures was taken on a spectrograph which was made in the Seemann Laboratories at Frieburg i. Br. The calibration of this spectrograph is described in the work of Slagle and Ott.[2]

The design and construction of our low temperature vacuum spectrograph follows. It is essentially a Bragg oscillating crystal spectrograph with the crystal table located at the center of a circle of approximately 18 cm radius and with the first slit located on the circumference and the photographic plate located as the tangent to a point 180° from the slit. The exposed plate area is 1×11 cm which allows reflections up to glancing angle $\theta = 9°$ to be observed on either

[4] Meyer and Reid, J. A. C. S. **55**, 1574 (1933).

[5] Andrews, Kohman and Johnston, J. Phys. Chem. **29**, 914 (1925).

[6] Manne Siegbahn, *Spektroskopie der Röntgenstrahlen*, Berlin, Julius Springer, 1931.

[7] The construction of the low temperature spectrograph was not absolutely necessary for the study of the alcohol series alone, but was essential for studies of other series with lower ranges of melting points such as the bromides and acetates, which are being made in this laboratory. The present work shows the applicability of this spectrograph to such studies.

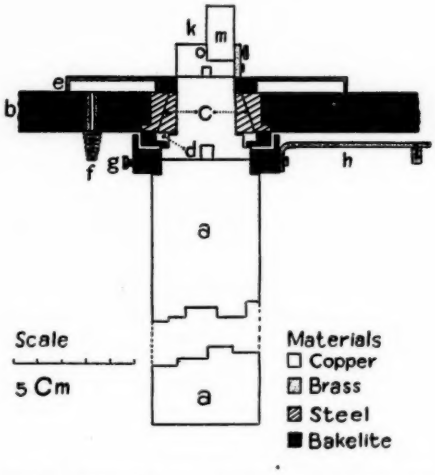

FIG. 1. Scale diagram of crystal table and cooling rod of the low temperature vacuum spectrograph.

side of the primary beam, which is a sufficient range for the purposes of this and following investigations. The arrangement of the recording photographic plate as a tangent does not impair the focussing, since the length of the plate is small as compared with the circumference of the circle. As a collimator, a system of two slits is used, the first being adjustable and made of a hard lead alloy while the second is fixed just in front of the crystal table and is made of steel. The oscillation of the crystal is accomplished by an eccentric cam arrangement driven by an electric motor.

The essential features of the cooling arrangement and crystal table are shown diagrammatically in Fig. 1. *a* is a solid copper rod which extends up through the floor *b* of the spectrograph and which is surrounded by a cooling mixture contained in a Dewar flask. The cooled portion is insulated as much as is possible with Bakelite parts. A lubricated steel on steel ground joint *c* affords the vacuum tight mechanism by means of which the oscillating motion is transmitted to the crystal table. The lubricating medium which is best suited for the carbon dioxide temperatures at which this work was being done is a mixture of a light aviation grade motor oil and a good grade gasoline in the ratio of 9 to 4. It is contained in the Bakelite reservoir *d* which acts in addition as a further protection against leakage. A brass shield *e* has the two-fold purpose of protecting the body of the spectrograph against oil seepage and to keep any air which might leak through the ground steel joint in as close contact as possible to the outlet *f* which leads to an ordinary oil vacuum pump. The crystal table *k* is so constructed that a solid block of copper *m* is forced against the ledge *o* by means of a set-screw holding the crystal plate tightly between the block and the ledge. Here, the plate is cooled by the copper block *m* which is in contact with the cooling rod *a*. *h* is the rocking arm which leads to the cam mechanism not shown here.

A mixture of CO_2 snow and acetone was found to produce a temperature of approximately $-50°C$ at the surface of the sample. On account of this low temperature, it was necessary to keep moisture from collecting on the surface of the crystal in some manner and this, in addition to reduced conduction of heat, was the reason for building the spectrograph with its vacuum feature. Under ordinary conditions of running, the amount of moisture which would collect on the crystal surface during a 16 hour period was barely noticeable. This, of course, is not sufficient to interfere seriously with ordinary x-ray reflection.

In order to know the temperature obtained in this manner, as well as to observe the constancy of this temperature with time, several cooling curves were plotted. The temperature was measured with a copper-constantin thermocouple, one junction of which was cemented to the surface of the crystal plate by means of universal wax. The cooling curves were made under as nearly as possible the same conditions as were met with in ordinary running. These curves proved that by refilling the Dewar cooling vessel at 2 hour intervals, a temperature constant to $\pm 1°$ was kept for any desired length of time.

It was necessary of course to calibrate the spectrograph, but it was impossible to do this in the same manner as was used to calibrate the Seemann spectrograph previously described, because the range of the glancing angle θ (0°–9°) observable on the plate is small and too close to the primary beam. This means that even with silver radiation and the mica 001 face, an insufficient number of reflections would be observed for accurate calibration. This difficulty

was surmounted by using as standard several long chain organic compounds whose spacings had been determined with known accuracy on the Seemann spectrograph in this laboratory. Three compounds were used, the C_{15} *n*-aliphatic acid, determined by Slagle and Ott[2] and the C_{17} and C_{18} *n*-aliphatic alcohols determined during the course of this work. The combination of these three substances gave a series of 19 points on the calibration curve, plotting distance in millimeters between corresponding lines on the film against the glancing angle θ. All fall accurately on a very smooth calibration curve which is nearly a straight line. The calibration curve is curved somewhat, since the photographic plate was placed as a tangent to the circle of focus rather than exactly on the circumference. The frame of the spectrograph is so insulated from the crystal table that its dimensions remain sufficiently constant under all running conditions. The entire work of calibration was performed at room temperature and so all of the spacings determined at the low temperature are referred to the calibration at room temperature. This fact allows comparisons to be made between spacings observed at $-50°$C and at room temperature and thus allows us to show the existence or non-existence of an expansion coefficient along the *c* axis.

The main body of the spectrograph was constructed of brass, with the exception of the floor which is of Bakelite and all the joints between brass and brass and brass and Bakelite were made vacuum tight with universal wax. The cover of the spectrograph and the brass plateholder were both cemented on with universal wax and were removed with lifting screws after air had been allowed to enter the spectrograph. The cover of the spectrograph was provided with a red glass window directly above the crystal table by means of which the rotation of the crystal could be observed. The 180°-rotation is accomplished by loosening the set-screw *g* (Fig. 1) and applying a specially constructed wrench to the cooling rod *a*.

Although the point has not been tried, there is no reason to doubt that the spectrograph could be used to investigate the behavior of long chain compounds through a wide range of temperatures by substituting for the CO_2-acetone cooling mixture anything from liquid air to a thermostatic arrangement for temperatures not too high above room temperature. It would only be necessary in each case to find the correct lubricant for the rotating joint. The constancy of the temperature at the surface of the sample suggests that the spectrograph could be used to investigate behavior near melting points, the phenomenon of molecular rotation or in general, transition points of all kinds.

The general method of calculating the *c* spacings from the films has been previously outlined. The distance *l* between corresponding lines on either side of the primary beam was measured by a micro-comparator in the case of the strong reflections and with a millimeter rule in the case of the weaker reflections. It was generally possible to measure the first, third and sometimes the fifth orders with the comparator. In each case, five separate readings were made of each order and the average taken as the final average *l*. Since plates were used in the low temperature spectrograph, it was not necessary to correct for shrinkage, but in the case of the Seemann spectrograph, which required films, this was necessary. The correction was made by making parallel scratches on the film before exposure, a known distance apart and then measuring the distance between these scratches just before measuring. The average *l* was then corrected, proportional to the amount of this shrinkage.

Having *l*, the distance between corresponding lines, accurately measured for several orders, it remains to find the glancing angle θ. The calibration curves for the two spectrographs were made by plotting *l* against θ and so θ is obtained simply by reading from the calibration curve. Now, knowing θ for a variety of orders, $\sin\theta$ can be found and by knowing *n* the order of reflection, from observation, $(\sin\theta)/n$ is found which reduces the sine values of the reflections from higher orders down to $n=1$. The variation in these values of $(\sin\theta)/n$ then gives us the maximum error in the calculation of *d*, the interplanar distance, which is obtained simply by substituting the average $(\sin\theta)/n$ value in Bragg's formula. Since $(\sin\theta)/n$ is averaged over several orders, the maximum deviation from the mean which is given in connection with the

TABLE I. *Calculations of c spacings.**

Order of reflection	Seemann spectrograph				Low temperature spectrograph			
	$C_{15}H_{31}OH$ (α)		$C_{18}H_{37}OH$ (β)		$C_{12}H_{25}OH$ (α)		$C_{13}H_{27}OH$ (α)	
	$\frac{\sin\theta}{n}$	Deviation (%)	$\frac{\sin\theta}{n}$	Deviation (%)	$\frac{\sin\theta}{n}$	Deviation (%)	$\frac{\sin\theta}{n}$	Deviation (%)
1	0.01825	−0.05	—	—	0.02252	+0.044	—	—
2	0.01828	+0.075	0.01876	−0.107	—	—	0.02081	−0.144
3	0.01826	0.00	0.01876	−0.107	—	—	0.02083	−0.048
4	0.01828	+0.075	0.01882	+0.212	0.02264	+0.57	0.02087	+0.144
5	0.01826	0.00	0.01878	0.00	0.02242	−0.38	0.02085	+0.048
6	0.01826	0.00	0.01881	+0.10	0.02246	−0.22	0.02083	−0.048
7	—	—	0.01878	0.00	—	—	—	—
8	0.01827	+0.05	—	—	—	—	—	—
Average $\frac{\sin\theta}{n}$	0.01826		0.01878		0.02251		0.02084	
$d=c$	42.12±0.05		40.96±0.10		34.17±0.32		36.91±0.05	

* It must be remembered that the *c* spacings calculated in this manner are not to be confused with the regular *c* spacings along the crystallographic *c* axes. The two are identical only when the *c* axis is perpendicular to the glass plate and hence to the 001 plane. These *c* spacings are a measure of the projection of the true *c* spacings on a line perpendicular to the 001 plane which appears to be parallel with the plane of the glass plate.

determination of *d* is probably much greater than the average error or the most probable error. However, in this work, it was thought best to give the variation in terms of the maximum deviation rather than the error, since the number of observations is relatively small.

In Table I are placed the calculations of films obtained from $C_{15}H_{31}OH$ and $C_{18}H_{37}OH$, respectively, by using the Seemann spectrograph. They represent one of the least and one of the most favorable cases and are typical of the accuracy obtained and the type of calculation. Likewise, Table I contains similarly representative calculations made from diagrams obtained on the low temperature spectrograph. These are $C_{12}H_{25}OH$ and $C_{13}H_{27}OH$, respectively. The table of calculations is self-explanatory.

In order to show the sharpness of reflection with which we are dealing and the type of films obtained, Fig. 2 shows several representative films made on the two spectrographs. The low temperature films, while easily measurable, do not reproduce well.

The final calculated values for the *c* spacings of all these aliphatic alcohols are given in Table II. In this table are also included Malkin's values for comparison. As will be seen later, these values indicate two distinct modifications of the *n*-alcohols. Quite arbitrarily, that modification which gives the longer spacing is called the α-modification whereas the one with the shorter spacing is called the β-modification.

DISCUSSION

If we compare *c* spacings as obtained from pressed samples with those obtained from crystallized or melted samples, we see that occasionally the agreement is not good. Of the two values, the spacing obtained from the pressed sample is likely to be in error. This is because the pressed sample is thicker, presents a more uneven surface, and as Slagle and Ott[2] have shown is likely to give spacings varying with the amount of pressure put upon the sample. As will be seen in Table II, the spacings observed in this work do not always agree with those published by Malkin[3] even within the maximum experimental deviation. This is probably not due to an inherent error in the methods used in the two investigations (although it is believed that the accuracy has been increased in this laboratory) but can be attributed to the presence of impurities in the alcohol in question. As explained before, the purity of the alcohols used in this

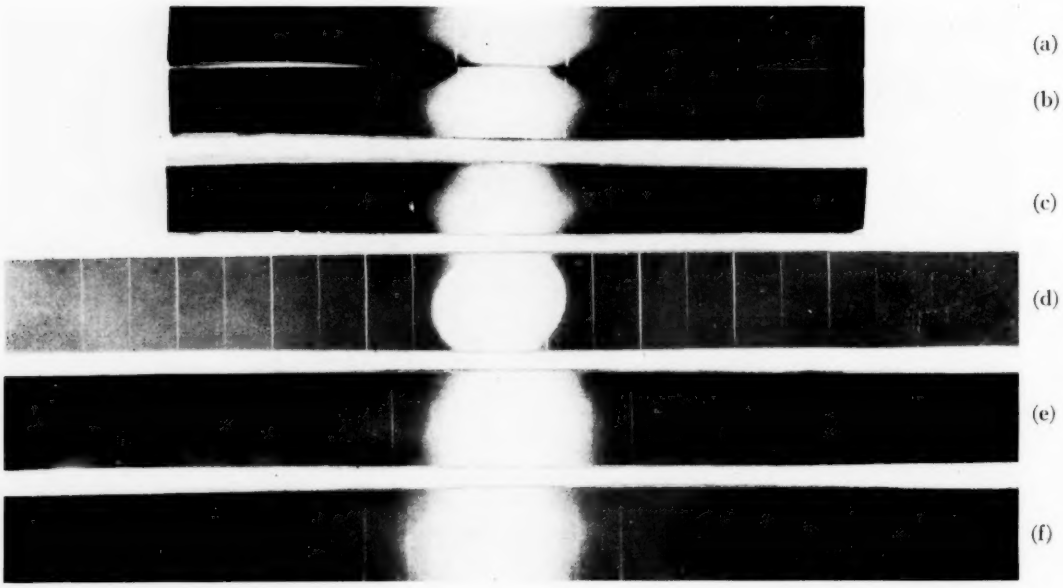

FIG. 2. X-ray diagrams taken on the two spectrographs used in this work. Diagrams (a), (b) and (c) were taken on the low temperature spectrograph while diagrams (d), (e) and (f) were taken on the Seemann spectrograph.

(a) $C_{14}H_{29}COOH$—room temperature
(b) $C_{14}H_{29}COOH$——50°C
(c) $C_{17}H_{35}OH$——50°C—α-modification
(d) $C_{16}H_{33}OH$—β-modification
(e) $C_{15}H_{31}OH$—α-modification
(f) $C_{14}H_{29}OH$—α-modification

work is unusually high and consequently the values given here are considered the more correct.

As in the case of the fatty acids, it is evident that the alcohol molecules crystallize in a double arrangement of some kind, probably with the hydroxyl groups adjacent to each other. The lengths of the c spacings as well as the increase observed for consecutive members of the series are much too great to be explained in any other manner. This viewpoint is supported by evidence in the paper following calculating intensities of reflection from assumed atomic arrangements.

Some of the diagrams show the presence of two modifications. This is clearly brought out if we plot the c spacings against the number of carbon atoms, in the usual manner. The graph, shown in Fig. 3, is made up of the c spacings obtained both by Malkin and the present authors. It therefore serves as a comparison of the two sets of values. The modification giving values which fall on the upper line is the α-modification while values which fall on the lower line belong to the β-modification.

It is interesting to note that in all of this work, there have been only two modifications observed as contrasted with the case of the fatty acids which show four and possibly five different modifications[2] in either even or odd series. In all cases the reflection from the α-modification is the more pronounced, when both appear on the same film. However, in the case of some preparations of the C_{16} and C_{18} alcohols, the presence of the β-modification only was observed. Reference to Fig. 3 will show that the β-modification has appeared only in the cases where the alcohol has an even number of carbon atoms. This is probably due to some difference in the ease of packing for even and odd molecules. That there is a difference in the packing of the α- and β-modification is indicated by a quite different relation between intensity and order of reflection.

Meyer and Reid[4] working with this same series of alcohols have obtained evidence from cooling curves which they interpret as showing the existence of two modifications of both even and odd members of the series. Our failure to obtain two modifications in the case of the odd members may be due to one of two reasons; either in our method of preparing the sample

TABLE II. *Observed c spacings in A of n-aliphatic alcohols.**

No. of carbon atoms	Crystallized from ether	Pressed	Results of Malkin Melted	Results of Malkin Pressed
		Room Temperature		
13	36.88±0.07 (α)	36.89±0.07 (α)		
14	39.67±0.07 (α)	39.38±0.46 (α)		39.7 (α)
15	42.12±0.05 (α)	42.13±0.08 (α)		
16	44.62±0.05 (α) 36.97±0.03 (β)	44.70±0.25 (α) 36.95±0.30 (β)	44.9 (α) 37.4 (β)	
17	47.16±0.14 (α)	46.99±0.25 (α)		
18	49.54±0.12 (α) 40.96±0.10 (β)	41.25±0.09 (β)	50.2 (α)	41.35 (β)

No. of carbon atoms	Crystallized from ether	Melted	Pressed
		−50° Centigrade	
10		28.74±0.34 (α) 22.41±0.06 (β)	
11		31.28±0.36 (α)	
12		34.17±0.32 (α)	
13			36.91±0.05 (α)
14			39.38±0.19 (α)
15			42.16±0.25 (α)
16			44.84±0.11 (α) 36.84±0.20 (β)
17	46.93±0.03 (α)		
18	49.57±0.12 (α) 40.96±0.08 (β)		

* See note below Table I regarding *c* spacings.

the cooling was so rapid that the transition point was passed without any appreciable change and at the low temperature, the rate of transition is so slow as not to give the second modification in any appreciable quantity, or this second transition point is due to a change in the rotation of the molecule only which would have no effect on our x-ray diagrams but which would have a marked effect upon the specific heat. Which of these two explanations is the correct one can only be decided after further work.

From our series of values of *c* spacings, we can calculate the average increase in length as the number of carbon atoms increases. This value is 2.53A for the α-modification and 2.00A for the

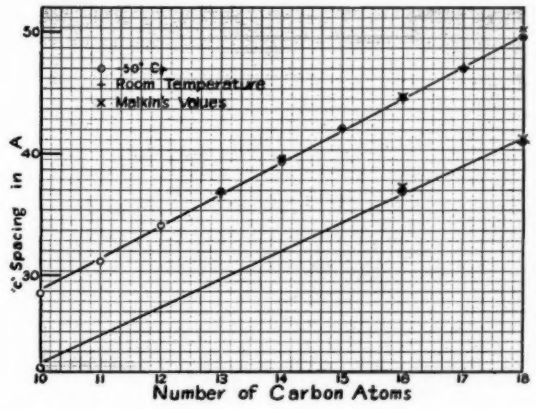

FIG. 3. Graph plotting *c* values against the number of carbon atoms in the hydrocarbon chain.

β-modification. Careful work with the hydrocarbons has shown that the increase in *c* spacing with the addition of two carbon atoms to the molecule is 2.54A. Since, in the modification of the hydrocarbons referred to, the *c* axis is perpendicular to the 001 plane, the correspondence between this value and our value would indicate that in the α-modification, the *c* axis is perpendicular to the 001 face. Likewise, the value of 2.00A increase per carbon atom found for the β-modification, when compared with 2.54A shows that the β-modification has the *c* axis tilted with respect to the 001 face. It is evident that the packing at the ends of the molecule would have no influence on this projected increase. Hence we can calculate the angle that the *c* axis makes with the 001 face in the case of the β-modification. If γ is this angle of tilt, simple geometrical considerations show that $\sin\gamma = 2.00/2.54 = 0.787$ and $\gamma = 51°\ 55'$, provided that we assume the chains in the case of the β-modification to be also parallel to each other. This would seem to be a reasonable assumption since the chains must be closely parallel to each other in the case of the α-modification. This is shown by the close check between the observed and calculated maximum increase along the *c* axis.

The tilt of the β-modification, when calculated in this manner, can then be used to show that the type of packing at the ends of the molecules must be different in the two modifications. This view, borne out further by the fact that the

relationship of the intensities of reflection is different in the two cases, has not hitherto been proposed. We know from the c spacing, the length of the projection of the total "double molecule." From the angle of tilt, we can easily calculate the value c would have for the β-modification, if the chain axis were perpendicular to the 001 face. This calculated c spacing should be the same as the c spacing for the α-modification if the packing were the same. The calculated c spacings for the β-modification are 46.99A and 52.04A for the C_{16} and C_{18} alcohols, respectively, while the corresponding c spacings for the α-modification which is perpendicular to the 001 plane are 44.62A and 49.54A. Although the experimental error in the determination of the c spacings is magnified in the value of $\sin\gamma$, we believe that this difference is real and not apparent and that it tends to strengthen our view that the packing is different in these two modifications.

If, in Table II we compare the c spacings obtained at room temperature with those obtained at $-50°$C, we fail to detect any difference, outside the experimental error. This means that the coefficient of expansion of these alcohols in the c direction is negligible. This compares favorably with the results obtained by Müller[8] in the case of the hydrocarbons. However, one acid was investigated in this manner and a change in the c spacing was observed. The C_{15} n-aliphatic acid, which was measured by Slagle and Ott[2] and used in the calibration of the low temperature spectrograph, gave a value at $-50°$C of 35.19 ± 0.10A as compared with 35.65 ±0.05A at room temperature. This is well outside the experimental error and gives a value for the coefficient of expansion of 0.00015A per A per °C. Although this shift in the c spacing with temperature lies outside the experimental error, the calculated coefficient of expansion should only be considered significant in order of magnitude because the experimental error is so large compared with the observed shift.

Because these alcohols are extremely simple as compared with other long chain compounds in regard to the possible number of modifications, they lend themselves very nicely to the study of mixtures and solid solutions. Some work along this line has been done by the authors but because of the fundamental nature of the problem, it was considered advisable to expand this work and publish it in a following paper.

[8] Müller, Proc. Roy. Soc. **A127**, 417 (1930).

Summary

(1) The c spacings of the series of n-alcohols $C_{10}H_{21}OH$ to $C_{18}H_{37}OH$ have been studied with improved accuracy.

(2) The n-alcohols crystallize in "double molecules" and the members with even numbers of carbon atoms exist in two distinct crystal modifications.

(3) These two modifications are shown to crystallize with the c axis making angles of 90° and 51° 55′, respectively, with the 001 planes and with the packing at the ends of the molecules likewise different in the two cases.

(4) A special spectrograph designed to permit such x-ray studies at temperatures below room temperature has been constructed.

(5) The results presented here are used in a following paper to determine atomic arrangements from intensity calculations.

A Calculation of the Intensities of Reflection of a Series of *n*-Aliphatic Alcohols*

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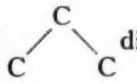
(Received February 9, 1934)

Comparison between observed and calculated intensities of c spacings of the α-modification of a series of n-aliphatic alcohols gives excellent values for the coordinates (projected on the c axis) of the constituent atoms.

IN 1925 Shearer[1] published a paper in which he attempted to explain the distribution of intensities of reflection with order from a number of long chain organic compounds. Because of later refinements in the theories of scattering, these calculations offer at best only a qualitative explanation of the phenomena. In the light of some of the observed reflections from long chain compounds used in this work, Shearer's results are actually in error. For these reasons it would seem advisable to use a more modern conception of such scattering and recalculate the intensities of reflection for some of the alcohols used here.

Suppose that instead of using a model such as Shearer proposed, we consider each atom along the chain as a diffracting center. Now if we draw a line parallel to the c axis of the crystal, we may project the centers of the atoms along the molecule on to this line and obtain an arrangement such as shown in Fig. 1. We may deal with this projected row of atomic centers as a row of diffracting centers and by finding the coordinates of each of these points along the line of projection, we may use the regular expression for the structural amplitude and thus calculate the intensities for various orders of the 001 reflections. This simplified arrangement is strictly rigid for such calculations.

In applying this general method to the case of the alcohols, let us see what dimensions or coordinates are unknown. As was previously shown,[2] the projected  distance is 2.54A and hence the projected distance is 1.27A for the α-modification which has the molecule chains perpendicular to the 001 plane. This gives us all the necessary dimensions relative to heavy atoms within the projected molecule except the projection of the distance. Atomic radii tables give the distance between oxygen and carbon centers as 1.42A.[3] This gives the projection of the distance as $1.42/1.54\times1.27 = 1.17$A for this linkage, assuming in this case also, the tetrahedral angle. Having these values, we see that there are but two unknown param-

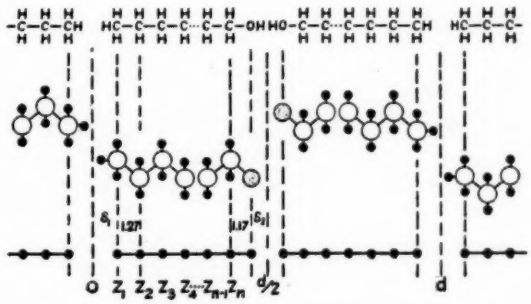


FIG. 1. Showing method of projection of the atoms along the n-alcohol chains.

* A portion of the thesis submitted by Donald A. Wilson to the Board of University Studies of The Johns Hopkins University in partial fulfillment of the requirements for the degree of doctor of philosophy.

† Pennsylvania state fellow under the National Fellowship Plan; holder of the John Wiley and Sons' fellowship.

[1] Shearer, Proc. Roy. Soc. **A108**, 655 (1925).

[2] D. A. Wilson and Emil Ott, preceding paper, p. 231.

[3] M. L. Huggins, Chem. Rev. **10**, 427 (1932).

eters, δ_1 and δ_2 (their definition is evident from Fig. 1). δ_1 which measures the shift of the entire molecule along this axis of projection is considered unknown, then δ_2 is simply related to δ_1 as follows:

$$d=2\{\delta_1+(n-1)1.27+1.17+\delta_2\},$$

where d is the interplanar distance and n is the number of carbon atoms in the molecule.

Thus we see that in an aliphatic alcohol containing n carbon atoms, the carbon atoms are located at $\pm\delta_1$, $\pm(1.27+\delta_1)$, $\pm\{2(1.27)+\delta_1\}$, $\pm\{3(1.27)+\delta_1\}$, $\cdots$ $\pm\{(n-1)(1.27)+\delta_1\}$ and the oxygen atom is located at $\pm\{(1.27)(n-1)+\delta_1+1.17\}$. These values are obtained by finding the distance along the axis of projection of each diffracting center from the origin, placed at a center of symmetry of the "double molecule" for convenience. However, in the expression for the structural amplitude, it is necessary that these coordinates be expressed as fractions of d along the z axis and hence we must transform these coordinates to $\pm u$, $\pm\{1.27/d+u\}$, $\pm\{2(1.27)/d+u\}$, $\pm\{3(1.27)/d+u\}$, $\cdots$ $\pm\{(n-1)(1.27)/d+u\}$ for the carbon atoms and $\pm\{[(n-1)(1.27)+1.17]/d+u\}$ for the oxygen atom when $u=\delta_1/d$. In all these considerations, the hydrogen atoms in each $-CH_2-$ group are considered as being projected to the same point on the axis of projection. This is merely done for convenience, since as is readily seen, the calculation remains rigid for 001 reflections. The $-OH$ group is treated as a single diffracting center while the end hydrogen on the hydrocarbon chain is neglected. This simplification can certainly introduce but a minor error.

These coordinates are then substituted in the expression for the structural amplitude,

$$S=2\sum_n F_n e^{2\pi i r z_n}=(A-iB),$$

where

$$A=2\sum_n F_n \cos 2\pi r z_n,$$

and

$$B=2\sum_n F_n \sin 2\pi r z_n,$$

where z_n is the fractional coordinate of the nth atom along the z axis, r is the order of reflection and F_n is the scattering factor for the nth atom. However, it is most reasonable to assume that the two alcohol molecules are arranged symmetrically about the origin, which is the center of the "double molecule" and corresponds to a center of symmetry in this case, since the molecule beyond the origin is the precise image of the one before it. The intensity is proportional to the square of the absolute value of the structural amplitude and is therefore proportional to A^2+B^2. However, now the term $B^2=0$ and so the intensity,

$$I\propto A^2\propto(2\sum_n F_n \cos 2\pi r z_n)^2$$

and because $B^2=0$ only cosine values need be considered and only positive values of the coordinates z_n are necessary. Nothing quantitative is known about the scattering factors for the carbon and oxygen atoms at such small values of θ, so as a first approximation, this factor was taken to be proportional to the atomic number, or 8 for the $-CH_2-$ groups and 9 for the $-OH$ group.

The F_n values for oxygen and carbon[4] in this region of small glancing angles actually do change and although the shape of the curve is not known accurately, we find that apparently to the first approximation it may be compared satisfactorily in our region with the curve of the function $1/\sin\theta$. With the rotating crystal method of analysis used in this work, it is necessary to introduce a correction factor $\sin\theta$ in calculating intensities since the area of crystal surface intercepting the x-ray beam increases as $\sin\theta$ and the energy striking the crystal surface must increase as that function. Consequently, it was thought that the value of this calculation would not be seriously impaired if these two corrections were allowed to cancel and only the relative heights of the two F_n curves for oxygen and carbon be applied as the scattering factors.

The intensity is then proportional to A^2 or to $(A/2)^2$, since any constant factor does not need to be included in a relative calculation and is equal to $f(\theta)(A/2)^2$ where $f(\theta)$ is a function of θ including the polarization, Lorentz and absorption factors. The value of $f(\theta)$ used is given

[4] R. W. G. Wyckoff, *The Structure of Crystals*, Chem. Cat. Co., (1931).

by Wyckoff[4] and can be shown to be valid for this type of calculation.

Since this calculation is based on the assumption that the alcohol molecules crystallize in pairs with the polar $-OH$ groups adjacent it is perhaps necessary to justify this viewpoint. This idea has been held by organic chemists for some years as applicable to all such cases of long chain molecules bearing a polar group on one end. X-ray researches with fatty acids and particularly in the case of lauric acid,[5] have further justified this point of view, at least with the case of the acids. That the alcohols present an analogous case can be seen by comparing the forces of molecular cohesion,[6] that of the acids being about 8970 cal. per mole and that of the alcohols being about 7250 cal. per mole. Shearer[1] has presented a more complete justification of this assumption as a preface to his calculations. At any rate, the success of the present calculations gives evidence strongly in support of this primary assumption.

We can now state our complete expression for the calculation of intensities.

$$I=f(\theta)(A/2)^2,$$

$$I=\frac{1+\cos^2 2\theta}{\sin 2\theta}\left[\sum_n F_n \cos 2\pi r z_n\right]^2. \qquad (1)$$

This expression can be criticized only from the point of view that the Darwin "extinction coefficient" of absorption has been neglected. The extinction coefficient does not become appreciable until we deal with reflections which lie exceedingly close to the primary beam, such as the first, second and possibly the third orders of reflection as observed in this work. This fact is used later to explain slight disagreements between observed and calculated intensities in the first two or three orders.

The C_{17} alcohol was chosen first for calculation for two reasons; first because reflections from this alcohol have been observed to higher orders than for any of the others and secondly because the c spacing obtained for this member is "average" in that the value falls accurately on the curve, plotting c spacings against the number of carbon atoms.[2] (See Fig. 2.)

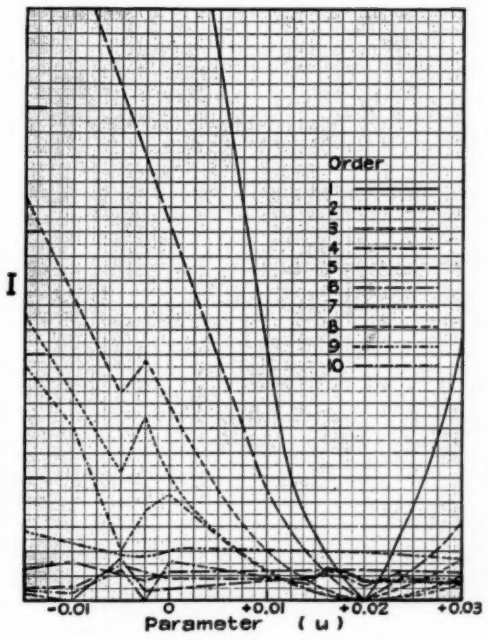


FIG. 2. Calculated intensities plotted against parameter values for the C_{17} alcohol.

The coordinates of each carbon and oxygen atom in the chain are found in the manner presented. The $-CH_2-$ groups can be placed at

u, $(0.02692+u)$, $(0.05385+u)$, $(0.08078+u)$, $(0.10771+u)$, $(0.13464+u)$, $(0.16157+u)$, $(0.18850+u)$, $(0.21543+u)$, $(0.24237+u)$, $(0.26929+u)$, $(0.29622+u)$, $(0.32315+u)$, $(0.35008+u)$, $(0.37701+u)$, $(0.40394+u)$, $(0.43087+u)$ and the $-OH$ group at $(0.45568+u)$. Thus $u=\delta_1/d$ is the only unknown parameter. It was determined by making preliminary calculations of the intensities, by using values of u increasing regularly on each side of the origin. Having obtained in this way a series of calculated intensities varying with the parameter u, the next step was to plot these calculated intensities against the parameter u for each order. That value of u which was found to give the proper sequence of relative intensities for the various orders, as compared with the experimental data, was found to be a singular value at $u=+0.027$.

[5] *Strukturbericht*, Leipzig, (1931).

[6] K. H. Meyer and H. Mark, *Der Aufbau der Hochpolymeren Organischen Naturstoff*, Leipzig, (1930).

TABLE I. *Calculated and observed intensities.**

Order of reflection	$C_{18}H_{37}OH$		$C_{17}H_{35}OH$		$C_{16}H_{33}OH$		$C_{15}H_{31}OH$		$C_{14}H_{29}OH$		$C_{13}H_{27}OH$	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
1	1614	500	1241	625	1180	320	1020	300	849	460	1161	385
2	312	250	349	200	354	165	371	150	419	230	251	200
3	526	500	385	500	355	320	300	300	246	460	341	350
4	155	150	224	175	225	160	183	120	246	200	150	150
5	255	250	200	225	161	160	81	250	127	230	176	190
6	155	50	146	200	121	115	66	90	137	140	120	150
7			124	125	99	100	104	60	48	90	98	70
8			150	175	168	165	161	120	181	185	114	115
9			72	50							54	60
10			174	175								

* The observed intensities listed here were estimated by direct visual observation. The error in such a method is about one part in ten and greater accuracy than this is not claimed.

With this value, the calculated intensities are found to be the values shown in Table I, where they may be compared with the experimental values.

The calculation is made simply by performing the designated operations in Eq. (1) for the intensity, summing the cosine values first over all the carbon atoms, then over the one oxygen atom, multiplying by the appropriate scattering factor F_n, completing the sum and squaring. The complete mathematical expression for the intensity of the C_{17} alcohol is

$$I=\frac{1+\cos^2 2\theta}{\sin 2\theta}\{8(\cos 2\pi r\,0.027+\cos 2\pi r\,0.05392+\cos 2\pi r\,0.08085+\cos 2\pi r\,0.10778$$
$$+\cos 2\pi r\,0.13471+\cos 2\pi r\,0.16164+\cos 2\pi r\,0.18857+\cos 2\pi r\,0.21550+\cos 2\pi r\,0.24243$$
$$+\cos 2\pi r\,0.26973+\cos 2\pi r\,0.29629+\cos 2\pi r\,0.32322+\cos 2\pi r\,0.35051+\cos 2\pi r\,0.37708$$
$$+\cos 2\pi r\,0.40401+\cos 2\pi r\,0.43094+\cos 2\pi r\,0.45787)+9(\cos 2\pi r\,0.48268)\}^2.$$

It is necessary to solve this equation for each order since r is the order of reflection and θ, the glancing angle, depends upon the order of reflection.

In order to compare these with the observed intensities, in Fig. 3 are shown diagrammatic representations of the calculated and observed intensities, with the absolute scale of each changed so that they are made to coincide insofar as possible. One will note that the agreement is very good indeed, particularly in the higher orders. It would be surprising if the first two or three orders were to coincide exactly because we have, as mentioned previously, neglected the "extinction coefficient" of absorption which becomes increasingly important in the low orders lying very close to the primary beam.

Let us see what this calculation tells us about the structure of this α-modification. In the first place, we have assumed that the chain axis was perpendicular or very nearly so with the 001 plane. The success of this calculation tends to substantiate this assumption. Since we have found $u=0.027$ in this manner and since $u=\delta_1/d$, we can find δ_1 which turns out to be 1.273A. This value is the distance from the origin to the center of the first carbon atom projection, which tells us that the projections of two molecules along the c axis have a distance of 2.55A between projections of the carbon centers on the ends opposite the hydroxyl groups. Solving for δ_2 then gives us the distance between the projection of the hydroxyl group and the point $d/2$. This value of δ_2 is subject to some variation due to inaccuracies in

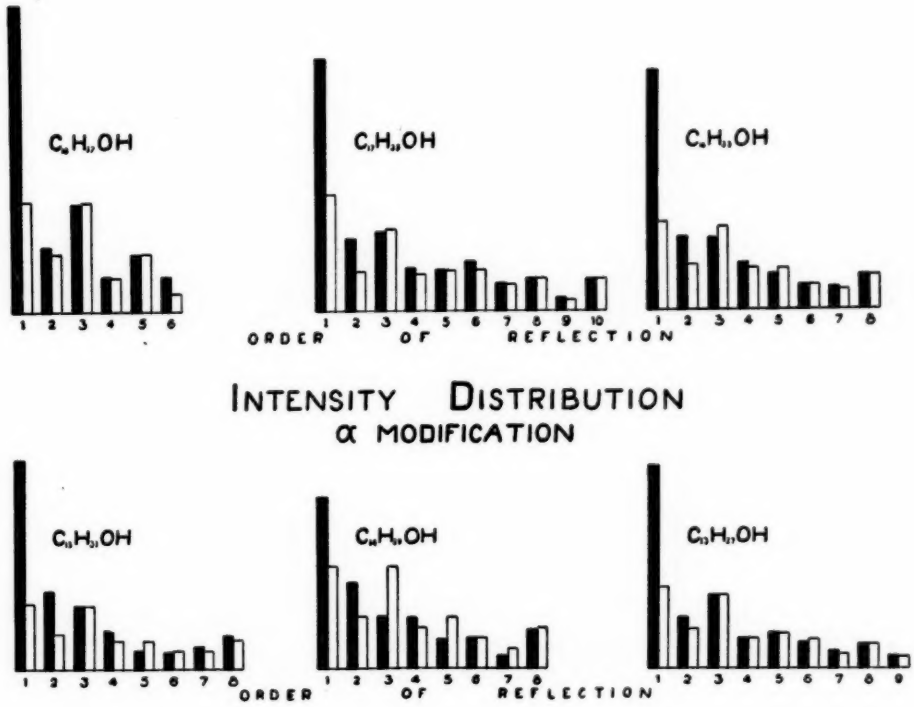


FIG. 3. Calculated intensities compared with observed intensities. The shaded values indicate calculated intensities.

the experimental determination of d, but when calculated for all the available alcohols in the α-modification, the results shown in Table II are found.

TABLE II. *Calculated values of* δ_2.

Alcohol	C_{18}	C_{17}	C_{16}	C_{15}	C_{14}	C_{13}	C_{12}	C_{11}	C_{10}
δ_2	0.737	0.877	0.807	0.837	0.877	0.753	0.667	0.497	0.497

Average $\delta_2 = 0.73A$

$2\delta_2$ is, of course, the distance between the projections of neighboring $-OH$ groups. The fact that all the variation due to experimental error in the determination of d seems to appear in the value of δ_2, is only apparent, because the calculation could just as easily have been made using the point $d/2$ as the origin which would have caused δ_2 to appear invariant. It is readily seen that the same experimental error is inherent both in δ_1 and δ_2.

So far we have derived all these quantities from the parameter found by calculating intensities for only the one alcohol $C_{17}H_{35}OH$. Precisely the same calculation, by using the same parameter values, should be applicable to the other members of the α-modification. The possibility of a change in the packing of the end groups from one member to another is quite remote, because not only do the c values all fall quite accurately on the same straight line[2] but the observed intensities all show the same type of alternation (Fig. 3). Thus, if we use the parameter $\delta_1 = 1.273$ with $\delta_2 = 0.73$ and apply the calculation to other members of this series and if the calculated intensities again check the experimental, this would offer good evidence in support of the theory. Such calculations have been made for the C_{13}, C_{14}, C_{15}, C_{16} and C_{18} members which give the calculated intensities shown in Table I and when the comparison of the intensities is shown diagrammatically as in Fig. 3, the results are good; in fact the agreement is even better in some cases than with the C_{17} alcohol.

Work is now in progress in this laboratory attempting to calculate intensities in a similar manner for the β-modification. The results are

promising but the calculations are complicated by the presence of two parameters, one measuring the angle of rotation of the molecule around its long axis as well as the one measuring the position of the projection of the molecule on the perpendicular. This new parameter arises from the fact that the c axis of the β-modification is tilted with respect to the 001 plane and consequently the projections of the individual atoms along the chain change their relative positions as the molecule is rotated.

It should be possible to extend the theory here presented to the calculation of intensities of reflection for all the long chain compounds, although many of the others offer complications which are not present in the case of the alcohols such as tilt, double bonded oxygens and so on. However, if the proper assumptions are made, it should be possible to extend this or a similar calculation to all cases.

Experimental Measurement of the Lattice Energies of RbBr and NaCl*

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(Received January 26, 1934)

By measuring electrically the ion emission through an orifice in an equilibrium chamber at high temperature containing salt vapor the lattice energies are calculated. The values obtained are 151.3 kcal. for RbBr and 181.3 kcal. for NaCl. The probable error is about 3.0 kcal. for both measurements, and the maximum error in the neighborhood of 7.5 kcal. The corresponding electron affinities are 84.2 kcal. for Br and 88.3 kcal. for Cl.

INTRODUCTION

BECAUSE of the interest to chemists of the Born cycle for the calculation of energies involved in the formation of ionic salts, the experimental determination of the lattice energies of some alkali halides has been undertaken to extend the original work of one of us on KI and CsI.[1] Further improvements in the theoretical calculation of lattice energies[2,3] have made desirable experimental work of the greatest possible accuracy.

The method used for the experimental determination is essentially as follows. By determining the current carried by ions flowing out of a measured hole in an oven containing salt vapor, the equilibrium pressures of ions P_+ and P_- of the ions M^+ and X^- in equilibrium with the gaseous salt vapor MX at a pressure P_{MX} are measured. From these data the free energy change, ΔF, and by calculation of the entropies the energy change, ΔE, of the reaction (1) $MX_{gas} \rightarrow M^+_{gas} + X^-_{gas}$ are calculated. By employing known energies of other reactions the lattice energy, ΔE for the reaction $MX_{Cr.} \rightarrow M^+_{gas} + X^-_{gas}$, (0°K) and the electron affinity of the halogen, ΔE for $X_{gas} + e^-_{gas} \rightarrow X^-_{gas}$ (0°K), may be calculated. The actual handling of the data used in this paper, although in principle assuming the same knowns as previously,[1] is such as to reduce greatly the uncertainty in the final lattice energies and electron affinities. The experimental procedure has also been greatly improved.

EXPERIMENTAL

The experimental arrangement has been altered from the original set-up of Mayer to give higher temperatures for the equilibrium (1) above. This was necessary in order to extend the measurements to the lighter alkali halides. One might instead use a more sensitive device for measuring the currents, but because of the difficulty of avoiding stray ion and electron currents this did not seem worth while. Modifications have also been made in the experimental technique to improve the accuracy of the experiments, since in Mayer's work the currents were not satisfactorily reproducible, and it seems probable, also, in view of our recent experiences that some unrecognized errors were inherent in the earlier procedure.

Fig. 1 shows the essential parts of the apparatus and may serve to illustrate how the measurements were carried out. The salt to be studied was placed in the lower half of the graphite oven (A) which was threaded into the upper part (B). (B) was heated directly by radiation. (A) was heated principally by conduction, so that its temperature could be adjusted by changing its position relative to the upper oven. The gaseous salt molecules, at a pressure determined by T_A, the temperature of the lower oven, diffused into B and then were

* From the dissertation submitted by L. Helmholz to The Johns Hopkins University in partial fulfillment of the degree of Doctor of Philosophy.

[1] J. E. Mayer, Zeits. f. Physik **61**, 798 (1930).

[2] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).

[3] J. E. Mayer and L. Helmholz, Zeits. f. Physik **75**, 19 (1932).

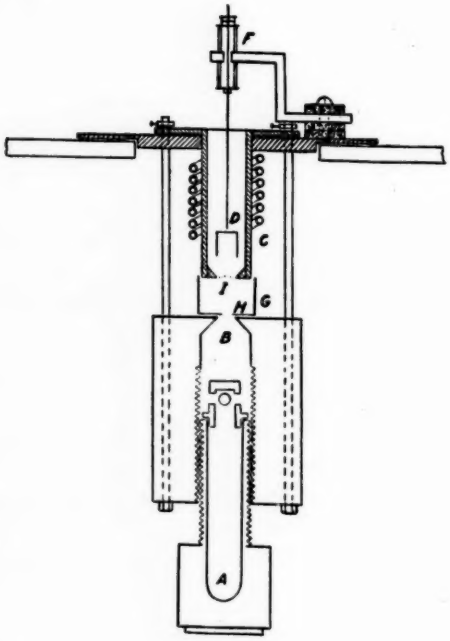

FIG. 1.

assumed to reach equilibrium with the ions and atoms at T_B, the temperature of the upper half.

The gaseous salt, ions, and atoms, diffused out of (B) through a measured hole in the platinum plate over a somewhat larger hole in the graphite oven. The pressure was such that Knudsen's equation could be used to calculate the numbers of ions diffusing out. The ions were caught by the Faraday cage D and the current measured by a sensitive galvanometer in series with it. A potential of a few volts was applied to the cage to collect either of the two ion types dependent on the sign of the potential.

The water-cooled shield C served to prevent ions and electrons from the heating elements and oven from reaching the cage, and also to select out a definite solid angle of the ion beam diffusing through H. Since salt collects on this part of the apparatus during an experiment the tube is water-cooled to prevent emission of ions or electrons from the surface which would otherwise be hot enough to permit this. A fine screen was placed at I to prevent the field of the Faraday cage from reaching through the opening and introducing uncertainty into the calculated solid angle of the ion beam that is collected. In practice the entire tube C was insulated and a potential applied to it; in this way it was possible at fairly low voltages (2–5 volts) to collect effectively the entire ion beam, since the ions emerge from the oven according to a cosine law and with velocities only as high as 0.05 volt. The screen removed 40 percent of the ion beam.

The Faraday cage was insulated by two pieces of quartz tubing held against a brass support as shown in the diagram. The rod to the cage was threaded and nuts tightened to hold washers against the quartz which in turn was held rigid with respect to the brass support. The support was insulated from ground by three glass plates which were kept cool during an experiment and were also out of the path of diffusing salt molecules, so could not become coated and give rise to surface conduction. After each run the cage was tested for electrical leak and always when cool found to be well insulated. It is possible, however, that occasionally when the system was hot the leak may have been appreciable. This would only materially effect the reading of low currents.

Fig. 2 shows the apparatus as a whole. The system is mounted on a steel plate to which a bell jar about 30 cm in diameter and 40 cm tall

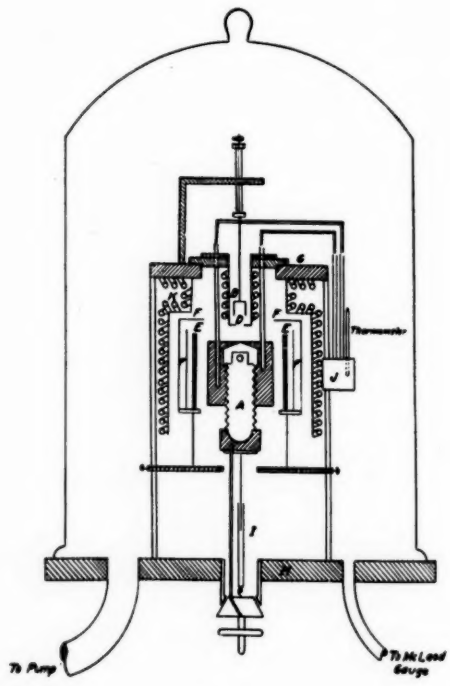

FIG. 2.

had been ground. With heavy grease it was found possible to hold the pressure to 10^{-4} mm Hg during runs with the temperature of the furnace as high as 1300°K. The leads are brought out through copper tubes soldered to the plate through Pyrex tubing held in place with picein.

A brass plate *G* held on three brass rods served to support the oven *A*, Faraday cage *B* and protecting tube *D* as well as the cooling jacket *K*. The cooling jacket was made from a large section of copper tubing 12 cm in diameter around the outside of which copper tubing was coiled and soldered in place.

The heating elements *E* of carborundum composition (Globar) were set in a framework which could slide on the three supporting rods and was capable of adjustment with respect to the oven. Six of the Globar rods, ground down to have a resistance of 30 ohms each, were mounted in parallel and gave fairly uniform heating at high temperatures. The resistance of these sticks decreases with temperature and they have the decided advantage over tungsten resistance elements that they are unaffected by residual oxygen pressure. Because of the amount of gas given off by the graphite furnace with rising temperature this fact was of great importance. As an example of the performance of the furnace: at 60 volts it carried 12 amperes and the oven temperature rose to 1225°K.

Several radiation shields (*F*) were interposed between the jacket and furnace to prevent loss by radiation. It was found particularly important to have the oven well shielded from above. Unless these precautions were taken differences of as much as 40° between the middle and the ends of the oven resulted.

The oven itself was turned out of a solid block of graphite with an outside diameter of 5 cm and drilled out on the inside to 1.5 cm. This gave a wall thickness that insured good conductivity and helped to prevent any large temperature gradient from the middle to the ends. In spite of this thickness and good shielding the differences rose as high as 10° at 1350°K. The influence of this on the results will be considered later. The lower half of the oven, also turned out of one block of graphite was 3 cm in diameter at the base with walls 1 cm thick, and served to keep the temperature of the solid salt fairly uniform. The threaded walls of the tube connecting it with the equilibrium chamber were only effectively 1.5 mm in diameter so that large temperature differences could be maintained between *A* and *B*. A small cap (shown in Fig. 1) was made to fit over the opening from *A* into *B* to prevent molecules from diffusing directly out of the oven without first suffering collisions with the walls in the upper oven.

C indicates the method by means of which the lower half of the oven could be raised or lowered during an experiment without breaking the vacuum. The iron rod screwed to the bottom of the furnace was connected to a ground joint fixed in the base plate by means of a surrounding tube in which it could slide.

Three thermocouples were employed to measure the temperature of different parts of the oven. They were C.P. platinum-platinum 10 percent rhodium couples and were calibrated at five points up to 1083°C and a table of deviations from the Bureau of Standards table recorded. One at a depth 1/3 and another at depth 2/3 of the oven were used in the upper part to determine the temperature of the equilibrium and to check the uniformity of the temperature along the length of the oven. The cold junctions of these thermocouples were insulated and fastened to a brass block attached to the inlet cooling water. A thermometer inserted in the block in the same way enabled us to make a correction for the difference in cold junction temperature from the standard. This was usually 20 or 25°C.

The system was evacuated with a three stage steel mercury diffusion pump which was, of course, in continuous operation. It reduced the pressure to 10^{-5} mm when the system was cold. The pressure was determined by means of a McLeod gauge attached to the system as shown in Fig. 2.

The galvanometer was the best Leeds and Northrup type M 8. rated at 10^{-11} amperes per mm scale deflection at 1 meter. As set up in this experiment it gave a sensitivity of 2.17 $\times 10^{-11}$ amperes per mm on calibration. The lead to the galvanometer was carefully insulated and came in contact with glass only when it emerged from the vacuum system. It was sealed in with de Khotinsky cement. The rubidium bromide used was Kahlbaums which had been crystallized

three times by Professor Jones and used in conductivity work in the department. The sodium chloride was used as a standard in x-ray analysis.

Calculation of Results

From the observed ion currents and the knowledge of the two temperatures T_A and T_B of the solid salt in A, Fig. 1, and of the vapor in B, as well as the geometry of the holes and measuring system, it is possible to calculate directly the lattice energy. For the reaction taking place at A, the sublimation of the salt, we have

$$F_A^\circ(MX_{\text{gas}}) - F_B^\circ(MX_{\text{cryst.}}) = -RT_A \ln P_{AMX} \quad (1)$$

and for the equilibrium at B,

$$F_B^\circ(\text{ion gas}) - F_B^\circ(MX_{\text{gas}}) = -RT_B \ln (P_+P_-/P_{BMX}) \quad (2)$$

where F_T° is the standard free energy of the indicated substance at the indicated temperature, and P_+, P_-, and P_{MX}, the pressures of the positive and negative ions and of the salt molecules (in atmospheres). It is assumed that due to the Knudsen effect $P_{AMX} = (T_A/T_B)^{\frac{1}{2}} P_{BMX}$.

Multiplying Eq. (1) by T_B and (2) by T_A and adding, the relatively uncertain value of P_{MX} is eliminated, and the less uncertain difference $T_BF^\circ_{T_A}(MX_{\text{gas}}) - T_AF^\circ_{T_B}(MX_{\text{gas}})$ introduced. For the various free energies the expression

$$F_T^\circ = E_0 + \int_0^T C_P dT - TS \quad (3)$$

is used, where E_0 is the energy at $T = 0°\text{K}$. The energy $E_0(MX_{\text{cryst.}})$, the energy of the crystalline salt at the absolute zero, is arbitrarily chosen as zero, E_0(ions), the energy of the ions at the absolute zero, is then the lattice energy. The specific heat integral of the salt is calculated from a Debye function, $RTD(\theta/T)$, $\theta = h\nu_{\max}/k$, and the entropy of the salt $RS_D(\theta/T)$ is similarly calculated assuming a Debye specific heat curve. Probable values for the $\nu_{\max}$ have been taken from an article by the authors.[3] E_0(sub.), the energy at 0°K of the gaseous molecule, has been taken from the same source, as have the probable values for the frequencies of the molecular vibration. These latter values for the gaseous molecules are all of negligible importance, since, as before remarked, only the difference of $TF_T^\circ(MX_{\text{gas}})$ at two not very distant temperatures enters the equation. If ϵ is the energy $h\nu$ of vibration of the gaseous molecule, the integrated specific heat due to vibration may be written $RTP(h\nu/kT)$ and the vibrational entropy $RS_E(h\nu/kT)$ where $P(h\nu/kT)$ and $S_E(h\nu/kT)$ are appropriate well-known functions. The equation for the lattice energy then becomes

$$E_0(\text{ions}) = -\frac{T_B - T_A}{T_A} E_0(\text{sub.}) + RT_B\left[\left\{P\left(\frac{\epsilon}{kT_B}\right) - P\left(\frac{\epsilon}{kT_A}\right)\right\} - \left\{S_E\left(\frac{\epsilon}{kT_B}\right) - S_E\left(\frac{\epsilon}{kT_A}\right)\right\}\right.$$
$$\left. + 6\left\{D\left(\frac{\theta}{T_A}\right) - S_D\left(\frac{\theta}{T_A}\right)\right\} - 7.314 + 1.5 \ln W_M W_X + 2.0 \ln T_B + 3.0 \ln T_A - \ln P_+P_-\right]. \quad (4)$$

W_M and W_X are the atomic weights of the two ions. The ionic gas is assumed to be unimolecular with only the Stern-Tetrode entropy.

The pressure of the gaseous ion is related to the galvanometer deflection by the relation

$$P_{\text{ion}} = \frac{(2\pi WRT_B)^{\frac{1}{2}}}{1.013\times10^6} \cdot \frac{2.17\times10^{-11}\times\delta}{A\times F\times 96{,}500} = 5.07\times10^{-18}(WT_B)^{\frac{1}{2}}\frac{\delta}{AF}. \quad (5)$$

Here δ is the galvanometer deflection in mm and 2.17×10^{-11} the sensitivity of the galvanometer in amperes per mm. A is the area in cm² of the oven opening, and F the calculated fraction of the ions recorded. F is of course dependent on the voltage placed on the screen and Faraday cage. The pressure is given in atmospheres. W is the atomic weight.

The pressures may be replaced in (4) by deflections, changing to $\log_{10}$ we obtain

$$E_0(\text{ions}) = -\frac{T_B - T_A}{T_A} E_0(\text{sub.}) + 4.598 T_B \Big[31.36 + \frac{1}{2.303} \Big\{ P\Big(\frac{\epsilon}{kT_B}\Big) - P\Big(\frac{\epsilon}{kT_A}\Big) \Big\}$$

$$- \frac{1}{2.303} \Big\{ S_E\Big(\frac{\epsilon}{kT_B}\Big) - S_E\Big(\frac{\epsilon}{kT_A}\Big) \Big\} + 2.605 \Big\{ D\Big(\frac{\theta}{T_A}\Big) - S_D\Big(\frac{\theta}{T_A}\Big) \Big\}$$

$$+ \log W_M W_X + \log T_B + 3 \log T_A + 2 \log A + 2 \log F - \log \delta_+ \delta_- \Big]. \quad (6)$$

This method of calculation, due to the partial elimination of the constants of the molecule gas, considerably reduces errors present in the original work on CsI and KI.

Discussion of the Method and Errors

In order to give an idea of the relative importance of the factors involved in the calculations the numerical values for experiment (1) in Table II are reproduced in Table I.

Table I.

$[(T_B - T_A)/T_A]E_0$ (sub.)	= 26.0 kcal.
4.598 T_B	= 6.04 kcal./2.303
numerical constant	= 31.36
log $W_M W_X$	= 3.83
log T_B	= 3.12
3 log T_A	= 8.80
$2.6[D - S_D]_{T=T_A}$	= −6.87
$(1/2.3)[(P_B - P_A) - (S_A - S_B)]$	= −0.12
2 log A	= −5.85
2 log F − log $\delta_+\delta_-$	= −4.68
sum	= 29.59
4.598 $T_B \times$ sum	= 178.5 kcal.
Lattice energy	= 152.5

It is evident that an error of 5 percent in $\int_0^T C_v dT - TS$ for the crystalline salt, corresponding to the same percentage error in $S(\theta/T) - D(\theta/T)$ would introduce about 2 kcal. error into the final lattice energy. This is possible, and the greatest single questionable item in the calculations alone. A fairly large error in the frequency of the gaseous molecule would have a negligible effect.

The 5 percent uncertainty (2.5 kcal.) in the energy of sublimation, E_0MX, introduces only 1 kcal. uncertainty in the lattice energy. About 3 kcal. maximum error, and probably considerably less, is then introduced by uncertainties in data unconnected with the experiment itself.

The temperatures are undoubtedly measured correctly in the experiment to better than 5°, which would introduce about 0.25 percent or about 0.5 kcal. uncertainty. Although the deflections are measured with considerable accuracy the fraction of the beam measured, and the diameter of the hole necessarily introduce some 25 percent error in this term, or about 1 kcal. in the lattice energy.

One may then expect a maximum error of ±3 kcal. due to uncertain values used in the calculations ±1.5 kcal. due to inherent experimental errors, *provided only* that the current measured is due to ions emitted from the oven and *provided* Eq. (5) relating the current measured to the pressure of ions in the oven holds correctly.

It is difficult to state exactly all the reasons adduced by the authors for believing that actually only ion currents from the oven were measured in the experiments reported. In various experiments not here reported stray currents undoubtedly existed. In many runs when salt had previously coated the outside of the oven at H in Fig. 1 abnormal positive currents and some negative currents were observed at even comparatively low temperatures. These currents dropped rapidly with time, presumably as the salt and other possible impurities distilled off the platinum plate. In other experiments when the shield G of Fig. 1 was absent abnormal stray currents were observed. Certain elementary reasons for believing that the currents observed in the reported experiments were due only to ions from the oven orifice may be given.

(1) The experiments were reproducible when no obvious difficulty arose.

(2) Without salt in the oven no deflections were observed. In one case during a run the salt

completely evaporated from the oven and the deflections fell to zero.

(3) Over a range of 125° and sevenfold change in current no systematic change in the calculated lattice energies is observable.

(4) Variations of the current with voltages applied to the screen I and Faraday cage D of Fig. 1 agreed qualitatively with the expected behavior of ions emerging from the hole H with about 0.05 volt energy and directions distributed according to a cosine law.

(5) Current with NaCl and RbBr in the oven differed by 35-fold in agreement with probable theoretical values of the lattice energies.

With regard to the second factor, the validity of Eq. (5) only negative remarks can be made. It is to be expected that what may be called a contact potential will exist between the gas in the interior of the oven and the platinum surface surrounding the hole H. An ion sheath will clothe the surface. An ion will then, depending on its sign, either be accelerated toward the hole H or repelled from it. It is consequently not to be expected that exactly equal numbers of negative and positive ions, or exactly numbers in the ratio of the square roots of the molecular weights, will emerge. For one ion species the deflection will be larger than that corresponding to the existing pressure, and for the other smaller. This effect is actually observed. The positive ion currents are always considerably larger than the negative ion currents, and the factor is in some cases as large as three. However, if this interpretation is correct the approximation of using the product of the two deflections in Eq. (6) will not be greatly in error. It is to be emphasized here that a threefold error in the estimation of the pressure of one of the ion species introduces only a 3 kcal. error in the final lattice energy, an error of 2 percent.

It is hoped that a slightly altered experimental technique and apparatus will enable us to completely obviate this uncertainty.

Little has been said in the above about the factor F in Eq. (5) giving the fraction of the ions caught by the Faraday cage. The screen I transmits only a certain fraction dependent on its transparency. If the true potential difference between H and I (Fig. 1) were exactly zero, a certain fraction calculable from cosine law emission and the geometry of the apparatus would hit the screen. As was to be expected this true zero of potential difference was found not to be zero as read on a voltmeter, but different (by 0.3 volt) due to the contact potentials and high temperature gradients existing at the connecting parts. If the potential of I were raised with respect to H (in either direction) one of the ion species would be accelerated perpendicular to the oven face and the fraction of these ions striking within the diameter of the hole at I should rise asymptotically to 1. This fraction should approach very nearly 1 at about 1 or 2 volts. This behavior was observed. By this method the authors believe that they were able to estimate the deflections when 100 percent of each of the ion species were striking within the hole radius I to within better than 20 percent.

Results

The result of 10 experiments on RbBr and 2 experiments on NaCl are given in Table II. The lattice energies of RbBr and NaCl deduced from the experiments, 151.3 and 181.3, respectively, agree well with the theoretical values 153.5 and 183.1 previously calculated by us.[3] The authors would be inclined to set an upper limit of 4.5 kcal. on the possible error of the experimental values, about 3 kcal. of which are due to uncertain data for the specific heat of the salts and the heat of sublimation. In addition there is, however, a *possible* error of some ±3 kcal. due to possible faulty interpretation of the results, which error, however, if it exists, will be

Table II. *Lattice energies of RbBr and NaCl.*

Salt	T_B (°K)	T_A (°K)	Deflections (δ_+ mm)	Deflections (δ_- mm)	Lattice energy (kcal.)
RbBr	1316	860	169	103	152.5
"	1319	868	188	116	153?2
"	1262	831	84	45	149.4
"	1260	837	91	32	152.2
"	1251	827	61	22	150.1
"	1244	830	39	14	152.0
"	1230	827	32	9	152.0
"	1226	827	31	6	151.7
"	1211	810	33	16	149.5
"	1197	824	25	15	150.2
NaCl	1264	945	13.5	11	181.7
"	1160	932	2.3	1.5	181.0

Average lattice energies, RbBr 151.3, NaCl 181.3 kcal.

systematic in the sense that it has the same sign and closely the same order of magnitude for both salts. The usual method of calculating probable error by root-mean-square method leads to ±2.5 kcal. neglecting the possible systematic error, and ±4 kcal. including this. Owing to the small number of experiments carried out on NaCl there is an additional uncertainty in this case.

With the Born cycle, and the particular values of ΔE for the involved reactions previously used by us, the electron affinity, ΔE for the reaction $X_{gas}+e^{-}_{gas}\rightarrow X^{-}_{gas}$ 0°K, is calculated to be 84.2 kcal. for Br and 88.3 kcal. for Cl.

The Mutual Repulsive Potential of Closed Shells[1]

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A method is developed for representing, in terms of a small number of integrals, the mutual potential of two ions or atoms having a rare gas electron configuration. The accuracy is the usual first approximation of the Heitler-London method. The integrals are evaluated for two like atoms, and numerical calculations made for two neon atoms. The total (repulsive) potential at $R=1.8\times10^{-8}$ cm is 344×10^{-14} erg; at $R=2.3\times10^{-8}$ cm, 35×10^{-14} erg; and at $R=3.2\times10^{-8}$ cm, 0.4×10^{-14} erg.

INTRODUCTION

THE calculation of the potential between two rare gas atoms by a generalized Heitler-London[3] method is a problem which in some respects is unique. First, the absence of degeneracy makes the solution comparatively simple in spite of the large numbers of electrons. Secondly the results are, almost without alteration, applicable to the repulsive potential between ions having a rare gas electron configuration, and so refer to a large number of chemical compounds. Thirdly, the experimental conditions under which this potential is observed: comparatively large distance between the ions and consequently low values of the potential, and in crystals symmetric surroundings for the ions leading to a minimum of distortion; lead one to believe that the theoretical calculations should give fairly accurate agreement with observed potentials.

The mutual potential of two helium atoms has been calculated by Slater[4] and others, but no adequate treatment has been given for the case of eight electrons.

In this paper the potential for two atoms or ions having closed shell configurations of eight electrons is represented in terms of a comparatively small number of integrals. The evaluation and numerical calculations are carried out for the case of two neon atoms. In a subsequent paper semi-empirical approximations of the integrals will be given which enable a simple and moderately accurate functional representation of the repulsive potential of two (rare gas shell) ions with known outer electron distribution.

THE INTEGRALS

The potential is determined as a perturbation energy of two atoms in a manner exactly analogous to the method of Heitler and London.[3] Two atoms a and b of core charge z_a and z_b, assumed to be point charges, have a nuclear separation R. There are sixteen electrons (twelve p and four s electrons) numbered from 1 to 16.[5] r_{ak} and r_{bk} are used as symbols for the distances from the nuclei a and b respectively to the electron k. The zeroth order wave function is a linear combination of permutations of the product of one-electron hydrogen-like functions,

[1] From a dissertation submitted by W. E. Bleick to the Board of University Studies of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] J. T. Baker Chemical Company Fellow.

[3] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).

[4] J. C. Slater, Phys. Rev. **32**, 349 (1928).

[5] In order not to make the succeeding mathematical presentation too cumbersome 8 electrons and a core charge (+8 for neutral atoms) are used instead of the more exact treatment with all electrons. The final results are so simple that the exact equations can be written readily. The extra integrals which would be introduced by the inclusion of the electrons underlying the closed shells can be seen to be negligible. The integrals which are evaluated, however, are modified to allow for the existence of the inner electrons.

$$\Psi_0=(1/16!)\sum_{P}^{16!\text{ terms}} c_P\Psi_P, \qquad \Psi_P=P(\Psi_1),$$
$$\Psi_1=\psi_{a0_s}\alpha(1)\cdot\psi_{a0_s}\beta(2)\cdot\psi_{a-}\alpha(3)\cdot\psi_{a-}\beta(4)\cdot\psi_{a0_p}\alpha(5)\cdots\psi_{a+}\beta(8)\cdot\psi_{b0_s}\alpha(9)\cdots\psi_{b+}\beta(16), \tag{1}$$

where ψ_{a0_s}, ψ_{a-}, ψ_{a0_p} and ψ_{a+} are the ns and np one-electron (Hartree) functions of atom a with $m_l=0_s$, -1, 0_p and $+1$, respectively, and α and β represent the two possible spin functions. The zero m_l's are given the subscript s or p according as the m_l refers to an s or p state.

P is a permutation operator, operating on the product of the 16 different functions of the sixteen electrons; 16! different permutations of the 16 electrons among the 16 functions are possible. c_P has the value $+1$ when the permutation P is even, and -1 when P is odd. The symbol Ψ_1 is used for the identical permutation of the product, written out as in Eq. (1), with electrons 1 to 8 on atom a, and 9 to 16 on atom b. Ψ_P is used for this product operated on by the permutation P.

The Schrödinger equation may be written

$$H(\Psi_0)=(T+V)(\Psi_0)=E\Psi_0. \tag{2}$$

The potential energy V has the form,

$$V=e^2\left[\sum_{k=1}^{k=16}{}'\sum_{l=1}^{l=16}\frac{1}{r_{kl}}-\sum_{k=1}^{k=16}\left(\frac{z_a}{r_{ak}}+\frac{z_b}{r_{bk}}\right)+\frac{z_az_b}{R}\right]. \tag{3}$$

If this value for V is substituted in (2) we may follow Heitler and London and cancel, in every permutation occurring additively in Ψ_0, the kinetic energy term plus that part of the potential energy which for the particular permutation occurs in the isolated atoms, operating on the permuted product Ψ_P with the sum of the energies of the two atoms $E_{0a}+E_{0b}$ multiplied by Ψ_P. There remains an equation in which the perturbation energy, and what may be termed a perturbation potential, occur. The form of the perturbation potential depends, however, on the permutation of the term Ψ_P which follows it. Calling ΔV_1 the perturbation potential for the identical permutation term Ψ_1, the perturbation potential ΔV_P for the term Ψ_P is obtained by operating on ΔV_1 with P.

$$\Delta V_1=e^2\left[\sum_{k=1}^{k=8}\sum_{l=9}^{l=16}\frac{1}{r_{kl}}-\sum_{k=1}^{k=8}\frac{z_b}{r_{bk}}-\sum_{l=9}^{l=16}\frac{z_a}{r_{al}}+\frac{z_az_b}{R}\right], \tag{4}$$

$$\Delta V_P=P(\Delta V_1). \tag{5}$$

The procedure outlined above leads to the equation,

$$(1/16!)\sum_{P}^{16!\text{ terms}} c_P\Delta V_P\Psi_P=\Delta E\Psi_0. \tag{6}$$

Multiplication by Ψ_0^* and integration over the whole space τ gives

$$(1/16!)\sum_{P}^{16!\text{ terms}}\sum_{P'}^{16!\text{ terms}} c_Pc_{P'}\int\Psi_P^*\Delta V_{P'}\Psi_{P'}d\tau=\Delta E\int\Psi_0^*\Psi_0d\tau=\Delta E(1-S). \tag{7}$$

S corresponds to the S of Heitler and London and has a small value ($\sim$0.01).

$$-S=(1/16!)\sum_{P}^{16!\text{ terms}}{}'\sum_{P'}^{16!\text{ terms}} c_Pc_{P'}\int\Psi_P^*\Psi_{P'}d\tau \tag{8}$$

in which $\sum'$ indicates that P and P' never take identical values. As will become evident later only permutations of one pair need be considered and the alternate Eq. (9) may be used,

$$S=2\sum_i\sum_j' S_{ij}, \quad \left(\begin{matrix}i\\ j\end{matrix}\right\}=0_s, -1, 0_p, +1\Big) \tag{9}$$

$$S_{ij}=|s_{ij}|^2$$

$$s_{ij}=\int \psi_{ai}^*\psi_{bj}d\tau,$$

i and j being indices that in this case indicate the value of the quantum number m_l.

The sum on the left of Eq. (7) contains $(16!)^2$ terms. After integration the numerical value of any term is, of course, independent of the numbers assigned to the electrons. We, therefore, change the notation of the electrons in each term taken as a whole, so that $\Psi_{P'}$ and $\Delta V_{P'}$ become Ψ_1 and ΔV_1, operating on the term with $(P')^{-1}$, obtaining 16! different terms each occurring 16! times. This gives

$$\sum_P^{16!\text{ terms}} c_P\int \Psi_P^*\Delta V_1\Psi_1 d\tau=\Delta E(1-S). \tag{10}$$

Of the 16! terms in Eq. (10) less than seventeen are different from each other and appreciably different from zero.

First since ΔV_1 is not a function of the spin coordinates and since α and β are orthogonal, $\int\alpha^*\beta=0$, terms in which any electron in Ψ_P^* has a different spin than in Ψ_1 are zero.

Secondly, since the perturbation potential contains no terms with the coordinates of more than one electron on the same atom in Ψ_1, and since $\int\psi_{ai}^*\psi_{aj}d\tau=0$ when $i\neq j$ all terms in which any electron has a different place (different ψ) *on the same atom* in Ψ_P^* and Ψ_1 are zero.

Thirdly, since the perturbation potential contains no terms with the coordinates of more than two electrons, and since $\int\psi_{ai}^*\psi_{bj}d\tau=s_{ij}\ll 1$ we may neglect terms in which more than one pair of electrons has different positions in Ψ_P^* and Ψ_1, because these will all be multiplied by factors $S_{ij}=|s_{ij}|^2\ll 1$.

Odd numbered electrons (spin α) may only be permuted with odd numbered electrons, and even with even. Fourthly, for every permutation of one pair of odd numbered electrons there will be a corresponding permutation of even numbered electrons in which electrons the same pair of functions ψ_{ai} and ψ_{bj} are permuted. The two terms will be numerically the same.

Of the 16! different terms Ψ_P^* we need now only consider the identical permutation Ψ_1^* and sixteen others. These sixteen others are those in which one of the four odd electrons (spin α) on atom a in Ψ_1 (electrons 1, 3, 5 or 7) is exchanged with one of the four odd electrons (spin α) on atom b in Ψ_1 (electrons 9, 11, 13 or 15). Each of these sixteen terms must be multiplied by a factor 2 to allow for the corresponding numerically identical term of electrons with spin β (even). The term of the identical permutation will have the plus sign for c_P; the other sixteen terms will have the minus sign.

Due to the analytical form of the functions ψ several of the sixteen terms will be numerically identical. For instance if the atoms a and b are the same, there are only seven different terms. If the permuted pair of electrons had both m_l's $=0_p$ one term results; and similarly if both m_l's $=0_s$. Two terms with the m_l's $=0_p$ and 0_s are identical. Four terms with the m_l's $=0_p$ and $+1$ or 0_p and -1 are identical; and similarly if the m_l's $=0_s$ and $+1$ or 0_s and -1. If both m_l's were $+1$ or both -1 the two terms are identical. Finally two terms with the m_l's $=+1$ and -1 are identical.

In order to further simplify the integrals it is necessary to introduce twelve new functions, six of the coordinate r_a the distance from the nucleus a, and six functions of the coordinate r_b. The functions are ρ_a, ρ_b, ρ_{ai}', ρ_{bj}', U_a, U_b, U_{ai}' and U_{bj}'.

ρ_a is the density of electric charge (in units of e) in the atom a. ρ_{ai}' is the density of charge in the atom a with the i'th electron of the closed shell missing. U_a is the potential due to atom a. U_{ai}' is the potential due to a when the i'th electron of the closed shell is missing. ρ_{ai}' and U_{ai}' are not to be confused with the corresponding functions of a singly charged ion of the element a, where the electron distribution has altered due to the altered field. They are calculated assuming the electron distribution of the atomic functions, neglecting one electron of the closed shell. Strictly speaking in the case of the

np electrons ρ_{ai}' and U_{ai}' are not functions of r_a alone, but also of θ_a and ϕ_a. They depend on the quantum number m_l of the missing electron. This neglect of the angular part of the function in the field is the same assumption that is made in the calculation of the Hartree functions which will be used in the evaluations.

The equations for ρ_a and ρ_{ai}' are the following:

$$\rho_a(r_a) = -\sum_{\text{all electrons}} |\psi_{ai}|^2 + z_a(\delta(r_a)/4\pi r_a^2), \quad (11)$$

$$\rho_{ai}'(r_a) = \rho_a + |R_{ai}(r_a)|^2/4\pi,$$

where $\delta(r_a)$ is Dirac's delta-function,[6] and $R_{ai}(r_a)$ is the radial function (normalized) of the i'th electron of the closed shell.

The potential $U_a(r_a)$ is given by

$$U_a(r_a) = \frac{1}{r_a}\int_0^{r_a} 4\pi r^2 \rho_a(r)dr + \int_{r_a}^{\infty} 4\pi r \rho_a(r)dr, \quad (12)$$

which is identical with

$$U_a(r_a) = z_a/r_a - \sum_{\text{all electrons}} \int \psi_{ai}^*(r_i)^{-1}\psi_{ai}d\tau_i, \quad (13)$$

where r_i is the distance from some point with the coordinate r_a to the i'th electron, and $d\tau_i$ is the volume element of the i'th electron.

The potential $U_{ai}'(r_a)$ is given by an equation identical with (12) in which ρ_{ai}' is substituted for ρ_a. This equation is identical with Eq. (13) in which the sum goes over all but one electron.

With the help of these functions, which it should be noted are easily calculated when the Hartree functions of the atom are available, we consider the seventeen terms of the sum on the left-hand side of Eq. (10).

The first term, in which the two identical permutations occur, is the classical Coulomb interaction, $e^2\int U_a\rho_b d\tau = e^2\int U_b\rho_a d\tau$. We may designate, in accordance with Heitler and London, this as W_{11}. It has a negative value in the range of R we are considering, occurs with a positive coefficient, and so leads to attraction.

The remaining exchange energy terms are not so trivially evaluated. Let us consider the term Ψ_P^* in which the electron pair $1 \leq i \leq 8$ and $9 \leq j \leq 16$ have exchanged the places they have in Ψ_1. All other electrons have the same positions (same ψ's) as in Ψ_1.

In this term we consider first those (additive) terms in ΔV_1, Eq. (4), which contain neither i nor j, that is where $k \neq i$, $l \neq j$. The partial integration of these terms gives

$$S_{ij}e^2\int U_{ai}'\rho_{bj}'d\tau = S_{ij}e^2\int U_{bj}'\rho_{ai}'d\tau.$$

The summation over all possible exchanges i and j gives $2e^2\sum_j\sum_j S_{ij}\int U_{ai}'\rho_{bj}'d\tau$. Since U_{ai}' and ρ_{bj}' do not differ greatly from U_a and ρ_b, and S is very small we introduce no great error by writing this SW_{11}. The terms all occur with a negative coefficient.

In the perturbation potential we have left the following terms: first $\sum_l'(r_{il})^{-1} - z_b/r_{bi}$, secondly $\sum_k'(r_{jk})^{-1} - z_a/r_{aj}$, and thirdly $(r_{ij})^{-1}$, where the symbol $\sum'$ is used to indicate that the sum over l does not include j, and the sum over k does not include i. The partial integration of the first of these terms gives $-s_{ij}e^2\int U_{bj}'\psi_{bj}^*\psi_{ai}d\tau$, and of the second $-s_{ji}e^2\int U_{ai}'\psi_{ai}^*\psi_{bj}d\tau$. The third term cannot be further simplified. All these terms occur with negative coefficient. ψ_{ai} and ψ_{bj} are the functions in which the electrons i and j occur in Ψ_1.

The results of these considerations are summed up in Eq. (14).

$$\Delta E = W_{11} - [2/(1-S)]\sum_i\sum_j (s_{ji}U_{ij}' + R_{ij}^{-1}), \qquad \binom{i}{j} = 0_s, -1, 0_p, +1\Big), \quad (14)$$

$$W_{11} = e^2\int U_a\rho_b d\tau = e^2\int U_b\rho_a d\tau,$$

$$U_{ij}' = -e^2\int (U_{ai}' + U_{bj}')\psi_{ai}^*\psi_{bj}d\tau,$$

$$R_{ij}^{-1} = e^2\int\int \psi_{ai}^*\psi_{bj}(1)(r_{12})^{-1}\psi_{bj}^*\psi_{ai}(2)d\tau_1 d\tau_2.$$

[6] P. A. M. Dirac, *The Principles of Quantum Mechanics*, p. 63, Oxford (1930).

The symbol $d\tau$ is used as elsewhere to indicate the volume element, and all integrations are to be carried out over all space. s_{ij} and S are defined in Eq. (9), and the U's and ρ's in (11), (12), (13).

To proceed further it is necessary to have analytical one-electron functions for the atoms a and b. That is, functions whose product satisfies the radial part of the Schrödinger Eq. (2) for the single atoms a and b, and which are orthogonal and normalized. Slater[7] has given such analytical approximations for the Hartree[8] functions. It is obvious that if the summation over i and j in (14) includes the inner electrons the expression is that which would be obtained if these electrons were not neglected. The expressions (11), (12) and (13) for ρ and U are taken to include all electrons. Actually it is here advisable, particularly in calculating U_{ai}' and U_{bj}', to include the inner electrons, and this does not add appreciably to the work of evaluation. It is, however, numerically unnecessary to include the inner electrons in the summation of (14). By the use of elliptic coordinates the calculation of W_{11} and U_{ij}' is straightforward and simple, although somewhat long. The calculation of R_{ij}^{-1} is difficult.

Neon Atom Functions

The Hartree field used for neon is that of Brown.[9] The following analytical representations of the $2p$ and $2s$ radial functions were employed:

$$R_{2p}(r)=r(17.9e^{-3.80r}+2.30e^{-1.69r}), \tag{15}$$

$$R_{2s}(r)=13.6e^{-8.22r}-r(14.7e^{-3.69r}+4.76e^{-2.15r}). \tag{16}$$

The $2p$ representation differs slightly from that given by Brown and is a better approximation to his calculated field for large radii. The unit of length in these and the following functions is the Bohr atomic unit, i.e., 0.528×10^{-8} cm.

Brown tabulates values of the charge density ρ and of the $2p$ and $2s$ radial functions. It is easy by substraction of $(2p)^2$ and $(2s)^2$, respectively, from ρ to calculate the modified charge densities ρ_{2p}' and ρ_{2s}' of (11). Approximate analytical representations of these densities are

$$\rho(r)=10(\delta(r)/4\pi r^2)-595e^{-19.3r}-r^2(155e^{-6.05r}+3.56e^{-3.47r}), \tag{17}$$

$$\rho_{2p}'(r)=10(\delta(r)/4\pi r^2)-613e^{-19.5r}-r^2(132e^{-5.99r}+2.88e^{-3.45r}), \tag{18}$$

$$\rho_{2s}'(r)=10(\delta(r)/4\pi r^2)-595e^{-19.3r}-r^2(134e^{-6.04r}+2.89e^{-3.41r}). \tag{19}$$

The integrations of ρ, ρ_{2p}' and ρ_{2s}' according to (12) and (13), yield the following potentials:

$$U(r)=-(20.0+2.08r^{-1})e^{-19.3r}+(53.2r^2+52.8r+26.2+5.77r^{-1})e^{-6.05r}+(3.73r^2+6.46r+5.59+2.15r^{-1})e^{-3.47r}, \tag{20}$$

$$U_{2p}'(r)=1/r+(20.2+2.07r^{-1})e^{-19.5r}+(46.1r^2+46.2r+23.1+5.15r^{-1})e^{-5.99r}+(3.04r^2+5.29r+4.60+1.78r^{-1})e^{-3.45r}, \tag{21}$$

$$U_{2s}'(r)=1/r+(20.1+2.08r^{-1})e^{-19.3r}+(46.1r^2+45.8r+22.8+5.02r^{-1})e^{-6.04r}+(3.13r^2+5.50r+4.84+1.89r^{-1})e^{-3.41r}. \tag{22}$$

Calculations

In the calculation of the integrals it is convenient to introduce the elliptic coordinates p, q defined by

$$p=(r_a+r_b)/R, \quad q=(r_a-r_b)/R.$$

As the third coordinate the azimuth ϕ about the line of nuclei is taken. The volume element is $(R/2)^3(p^2-q^2)dpdqd\phi$. It is assumed that the polar axis of each atom is directed toward the other atom along the line of nuclei. Then θ_a and θ_b, the angles between the radius vectors r_a and r_b respectively and the line of nuclei, are given by

[7] J. C. Slater, Phys. Rev. **42**, 33 (1932).

[8] D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89, 111 (1928).

[9] F. W. Brown, Phys. Rev. **44**, 214 (1933).

$$\sin\theta_a=[(p^2-1)(1-q^2)]^{\frac{1}{2}}/(p+q),$$
$$\sin\theta_b=[(p^2-1)(1-q^2)]^{\frac{1}{2}}/(p-q),$$
$$\cos\theta_a=(1+pq)/(p+q),$$
$$\cos\theta_b=(1-pq)/(p-q).$$

In these coordinates all of the integrals except R_{ij}^{-1} reduce to a sum of terms of the type

$$\int_{p=+1}^{p=\infty}\int_{q=-1}^{q=+1} p^n q^m e^{-\alpha p-\beta q}dpdq = (-1)^m(e^{\beta-\alpha}/\beta\alpha)A_n(\alpha)B_m(\beta), \quad (n, m\geqslant 0;\ \alpha>0),$$

where

$$A_n(\alpha)=\sum_{i=0}^{n} n!\alpha^{-i}/(n-i)!, \quad (23)$$

$$B_m(\beta)=A_m(-\beta)+(-1)^{m+1}e^{-2\beta}A_m(\beta),$$
$$B_m(-\beta)=(-1)^{m+1}e^{2\beta}B_m(\beta),$$

and α and β are proportional to R. The polynomials $A_n(\alpha)$ are conveniently calculated from the recursion formula

$$A_n(\alpha)=1+nA_{n-1}(\alpha)/\alpha. \quad (24)$$

The integrals R_{ij}^{-1} have been evaluated for the $2p$ electrons of like atoms and are given in an appendix.

Numerical Results

The numerical values of the integrals (9) and (14) for two neon atoms are tabulated in Tables I and II. The nuclear separation of 3.2×10^{-8} cm corresponds to the equilibrium separation of atoms in the neon lattice at the temperature of liquid helium. The separation of 2.3×10^{-8} cm is the same as the distance of closest approach of unlike ions in the sodium fluoride lattice at room temperature.

Discussion of the Results

Lennard-Jones[10] gives several choices of values for the three constants A, B and n of an empirical equation $\phi=-A/R^6+B/R^n$ for the total potential between two neon atoms as deduced from various experimental measurements. Two sets, $n=9$, $A=13.7\times10^{-60}$, $B=3.27\times10^{-82}$ and $n=12$, $A=8.45\times10^{-60}$, $B=36.3\times10^{-106}$, have been used to calculate the "experimental" values of the potential given in the first two columns of Table III. Needless to say the extrapolation of these equations to $R=1.8\times10^{-8}$ cm has not much value. In order to calculate the corresponding theoretical potential it is necessary to include a term which would be added by the second approximation of the method used here. At fairly large distances this term can be readily approximated, as shown by London,[11] using a development of the perturbation potential in R. The first term becomes $-A/R^6$, $A\leqq 3\alpha^2J/4$. α is the polarizability, and J an energy corresponding to the most intense absorption frequencies. Using $\alpha=0.392\times10^{-24}$ cm^3 and $J=25$ volts, $A=4.6\times10^{-60}$ erg cm^6. By adding this term to our previously calculated repulsion the third column of Table III is obtained.

TABLE I. *Numerical values of the integrals for two neon atoms.*

R (cm $\times10^8$)	i	j	s_{ij} ($\times10^2$)	S_{ij} ($\times10^4$)	$-U_{ij}'/e^2$ (cm^{-1} $\times10^{-4}$)	$-s_{ij}U_{ij}'/e^2$ (cm^{-1} $\times10^{-4}$)	R_{ij}^{-1}/e^2 (cm^{-1} $\times10^{-4}$)
	0_p	0_p	11.6	133	4184	483	203
	0_p	0_s	9.73	94.7	4174	406	116
	0_s	0_s	5.02	25.2	2069	104	30.8
1.8	±1	±1	3.87	15.0	1083	41.9	13.1
	0_p	±1	0	0	0	0	14.2
	±1	0_s	0	0	0	0	6.15
	±1	∓1	0	0	0	0	1.41
	0_p	0_p	5.43	29.4	1502	81.5	37.5
	0_p	0_s	3.42	11.7	1166	39.9	13.1
	0_s	0_s	1.31	1.71	412	5.39	1.91
2.3	±1	±1	1.24	1.54	263	3.26	1.23
	0_p	±1	0	0	0	0	1.67
	±1	0_s	0	0	0	0	0.403
	±1	∓1	0	0	0	0	0.129
	0_p	0_p	0.984	0.968	173	1.70	0.982
	0_p	0_s	0.410	0.168	102	0.418	0.162
	0_s	0_s	0.0930	0.00865	19.7	0.0183	0.00832
3.2	±1	±1	0.141	0.0200	21.4	0.0302	0.0138
	0_p	±1	0	0	0	0	0.0259
	±1	0_s	0	0	0	0	0.00245
	±1	∓1	0	0	0	0	0.00143

The certainty of the experimental values of the potential is somewhat less than that indicated by the agreement between the two columns of Table III. Obviously the attractive potential is actually greater than that used to calculate the column marked "theoretical." This is due partly to the rough approximation used to obtain the constant A, and partly to the neglect of higher order terms. Table III indicates, however, that the values of the repulsive potential calculated

[10] J. E. Lennard-Jones, Proc. Phys. Soc. **43**, 461 (1931).

[11] F. London, Zeits. f. physik. Chemie **11**, 222 (1930).

TABLE II. *Sums.*

R (cm$\times 10^8$)	S ($\times 10^3$)	$\frac{-2}{1-S}\Sigma_i\Sigma_j s_{ji}U'_{ij}$	$\frac{2}{1-S}\Sigma_i\Sigma_j R_{ij}^{-1}$	$\frac{-2}{1-S}\Sigma_i\Sigma_j(s_{ji}U_{ij}+R_{ij}^{-1})$	$-W_{11}$	ΔE
		(ergs$\times 10^{14}$)				
1.8	75.6	729	283	446	102	344
2.3	11.5	79.7	35.3	44.4	9.45	34.9
3.2	0.271	1.19	0.663	0.526	0.101	0.426

in this paper are not in definite disagreement with experiment. A much better comparison with experiment could, of course, be carried out if the repulsive potential between an alkali and a halide ion were calculated.

It is interesting to attempt to fit the values of Table II to a simple two constant equation. This has been done using the two extreme values to calculate the constants and comparing the equation with the value of Table II at $R=2.3$A. The equation $\varphi(R)=B/R^n$; $B=2.71\times 10^{-102}$ in ergs and cm, $n=11.63$, fits the two values at $R=1.8$A and 3.2A but gives 19.8×10^{-14} erg at 2.3A instead of 34.9×10^{-14}, a deviation of 40 percent. The equation $\varphi(R)=b\exp(2r_0-R)/\rho$, b arbitrarily chosen as 10^{-12} erg, $r_0=1.029\times 10^{-8}$ cm and $\rho=0.2091\times 10^{-8}$ cm fits the two values at 1.8 and 3.2A and gives 31.5×10^{-14} erg at 2.3A, an agreement to within 10 percent. Obviously the exponential equation gives a better fit than the inverse power.

TABLE III. *The total potential between two neon atoms.*

$R\times 10^8$ cm	*Potential, ergs*$\times 10^{14}$ Experimental $n=9$	Experimental $n=12$	Theoretical
1.8	124	289	331
2.3	8.9	10.9	31.9
3.2	−0.35	−0.47	0.00
3.5	−0.33	−0.35	−0.2
4.0	−0.21	−0.18	−0.1

The exponential equation above is of the form proposed by Born and Mayer[12] for the repulsion between alkali and halide ions, the value of ρ for all the alkali halides being 0.345×10^{-8} cm, and the comparable r_0 values for Na^+ ion and F^- ion being respectively 0.875×10^{-8} cm and 1.110×10^{-8} cm.[13] Presumably the more diffuse electron distribution function of the negative ion determines the steepness (the value of ρ) in the repulsion between the ions.

APPENDIX

The analytical expressions of the R_{ij}^{-1} integrals for the $2p$ electrons of like atoms are given here since they have not appeared previously in the literature in closed form. It is assumed that the normalized $2p$ radial function of both atoms is mre^{-kr} where m and k are constants. The integrals were calculated by using Neumann's[14] expansion in elliptic coordinates of the reciprocal distance $1/r_{12}$ between two points (p_1, q_1, ϕ_1) and (p_2, q_2, ϕ_2). This formula for the case $p_1>p_2$ is

$$\frac{1}{r_{12}}=\frac{2}{R}\sum_{\tau=0}^{\infty}\sum_{\nu=-\tau}^{\nu=+\tau}(-1)^\nu(2\tau+1)\left[\frac{(\tau-|\nu|)!}{(\tau+|\nu|)!}\right]^2 P_{\tau\nu}(p_2)Q_{\tau\nu}(p_1)P_{\tau\nu}(q_1)P_{\tau\nu}(q_2)e^{i\nu(\phi_2-\phi_1)},$$

where $P_{\tau\nu}$ and $Q_{\tau\nu}$ are the associated Legendre polynomials of the first and second kinds, respectively. For the case $p_1<p_2$ exchange the rôles of p_1 and p_2.

[12] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).
[13] M. Huggins and J. E. Mayer, J. Chem. Phys. **1**, 643 (1933).
[14] F. Neumann, *Vorlesungen über die Theorie des Potentials*, p. 341, Leipzig (1887).

The results are

$$R^{-1}_{0_p0_p}=4g\{147W[1(0,5,-18,5);0(\ \ )]+15W[1(21,-25,27,-7);6(7,-6,7)]$$
$$+W[3(35,-30,3,0);10(21,-11,0)]\},$$

$$R^{-1}_{\pm1\pm1}=g\{588W[1(0,5,-6,1);0(\ \ )]+15W[1(21,-25,3,1);6(7,-6,-1)]$$
$$+W[3(35,-65,33,-3);10(21,-32,11)]\},$$

$$R^{-1}_{0_p\pm1}=-140g\{9W[1(0,5,-6,1);2(0,5,-2)]+W[3(7,-10,3,0);2(21,-23,5)]\},$$

$$R^{-1}_{\pm1\mp1}=70gW[3(7,-15,9,-1);2(21,-38,9)],$$

where

$$g=3R^9(m^2e^{-\alpha}/53{,}760\alpha)^2, \qquad \alpha=kR,$$

$$W[c_1(a_6,a_4,a_2,a_0);c_2(b_5,b_3,b_1)]=c_1\{M^2(C+\ln\alpha)-2LMe^{2\alpha}Ei(-2\alpha)+L^2e^{4\alpha}Ei(-4\alpha)$$
$$-(1/2\alpha)\sum_{j=0}^{4}\sigma_j[2MA_j(\alpha)+\mu_j]+(1/2\alpha)\sum_{j=0}^{5}s_jA_j(2\alpha)\}$$
$$-c_2\{MN+(1/2\alpha)[(5b_5\mu_4+3b_3\mu_2+b_1\mu_0)-(6a_6\nu_5+4a_4\nu_3+2a_2\nu_1)]\}$$

and

$$L=a_6A_6(-\alpha)+a_4A_4(-\alpha)+a_2A_2(-\alpha)+a_0,$$
$$M=a_6A_6(\alpha)+a_4A_4(\alpha)+a_2A_2(\alpha)+a_0,$$
$$N=b_5A_5(\alpha)+b_3A_3(\alpha)+b_1A_1(\alpha),$$
$$M_i'=a_6A_{6+i}(2\alpha)+a_4A_{4+i}(2\alpha)+a_2A_{2+i}(2\alpha)+a_0A_i(2\alpha)$$
$$N_i'=b_5A_{5+i}(2\alpha)+b_3A_{3+i}(2\alpha)+b_1A_{1+i}(2\alpha),$$
$$\mu_i=M_i'+i\mu_{i-1}/\alpha, \qquad \mu_0=M_0',$$
$$\nu_i=N_i'+i\nu_{i-1}/\alpha, \qquad \nu_0=N_0',$$
$$A_{m,\,n}(\alpha)=A_m(\alpha)-m!\alpha^{n-m}A_n(\alpha)/n!, \qquad (0\leqslant n\leqslant m-1)$$

$$s_n=s_n(L,M)=\sum_{i=t}^{3}a_{2i}[MA_{2i,\,n}(\alpha)+(-1)^{2i-n}LA_{2i,\,n}(-\alpha)], \qquad t=(2n+3+(-1)^n)/4$$
$$\sigma_n=s_n(1,1).$$

The $A_j(\alpha)$ are the polynomials of Eq. (23) and $Ei(x)$ is the logarithmic-integral function.[15] C denotes the Euler constant 0.5772157.

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[15] For definition and tables of this function see E. Jahnke and F. Emde, *Tables of Functions with Formulae and Curves*, Second edition, p. 78, B. G. Teubner, Leipzig (1933).

On the Dispersion of Sound. Consideration of Three Energy Levels

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§1.

In a recent issue of this Journal there appeared a paper by W. T. Richards[1] on the dispersion of sound due to vibrational energy lag in a gas with several energy states in which the cases of two, three and four vibrational levels were treated. It is important to realize that to consider n levels including the ground state, and to neglect all higher levels is equivalent to neglecting all powers of the Boltzmann factor $\exp(-\epsilon/kT)$ higher than the $(n-1)$ st, ϵ being the energy difference between two adjacent states. Considering the case of three energy levels, the calculation of the velocity of sound must be carried out consistently in powers of this parameter of smallness so that in the final result no terms of higher order than the second are present. This point, it seems, has not been sufficiently recognized in the literature. In Richards' case this has apparently led to an improper choice of reaction equations.

§2.

Case of two energy levels. The dispersion of sound for the case of two levels has been carried out by Kneser[2] and Rutgers.[3] The method due to Einstein[4] is essentially as follows. The reaction to be considered is

$$\text{(a)} \qquad N_0+N_0 \rightleftarrows N_0+N_1,$$

where N_0, N_1 refer to a molecule in the ground state and first excited state, respectively. This leads to the reaction equation

$$V(dn_1/dt)=\kappa_1 n_0^2-\kappa_2 n_0 n_1, \tag{1}$$

in which V is the total volume, κ_1, κ_2 the reaction, rate constants characterizing the rate of energy adjustment for the forward and reverse reactions, respectively, and n_0, n_1 the total number of molecules in the states 0 and 1, respectively.

By the principle of detailed balancing the two parameters κ_1, κ_2 are not independent but are related by

$$\kappa_1/\kappa_2=\exp(-\epsilon/kT)=\mu.$$

The calculation of the velocity of sound f may be based on the characteristic acoustical equation

$$f^2=\text{real part } (p/\rho)(1-\Delta pV/p\Delta V), \tag{2}$$

p and ρ referring to the pressure and density, respectively, the displaced equation of state

$$\Delta pV=nk\Delta T \tag{3}$$

and the thermodynamic equation for adiabatic change

$$-p\Delta V=nC_\infty\Delta T+\epsilon\Delta n_1, \tag{4}$$

in which C_∞ is that part of the total specific heat per molecule which is independent of the frequency, and n is the total number of molecules in the gas.

Taking the time dependence of n_1 about its equilibrium value to be of the form $\exp i\omega t$, ω being the frequency of the sound wave in radians per second, the variation of (1) yields

$$\begin{aligned} i\omega V\Delta n_1&=\kappa_2 n_0[n_0\mu\epsilon\Delta T/kT^2-(\mu+1)\Delta n_1] \\ &\cong \kappa_2 n(n\mu\epsilon\Delta T/kT^2-\Delta n_1), \end{aligned} \tag{5}$$

where use has been made of the fact that $n_0+n_1=n=$ constant, and therefore $\Delta n_0=-\Delta n_1$; further $n=n_0(1+\mu)$.

Eliminating Δn_1 from (4) and (5) and combining the result for $\Delta T/\Delta V$ thus found with (2) and (3), the final expression for the frequency dependent velocity of sound is found to be

$$f^2(\omega)=\frac{p}{\rho}\left(1+\frac{k}{C_\infty}-\frac{\epsilon^2}{C_\infty{}^2T^2}\frac{1}{1+\omega^2V^2/\kappa_2{}^2n^2}\mu\right). \tag{6}$$

The result when expressed in this form puts in evidence the relative order of magnitude of the

[1] W. T. Richards, J. Chem. Phys. **1**, 863 (1933).
[2] H. O. Kneser, Ann. d. Physik **11**, 761 (1931).
[3] A. J. Rutgers, Ann. d. Physik **16**, 350 (1933).
[4] A. Einstein, Sitz. Ber. Akad. 380 (1920).

contribution to the sound velocity due to vibrational transitions and the part independent of such transitions. The presence of powers of μ only up to the first is an expression of the fact that only one excited level is considered. This seems to the writer to be the consequent form in which to write the result of Kneser and Rutgers.[5]

If the vibrational specific heat is calculated from

$$C_i=(d/dT)(\epsilon\mu/1+\mu), \tag{7}$$

then the expected result in the limiting case of small frequency

$$f^2(0)=(p/\rho)(1+k/C_\infty+C_i) \tag{6'}$$

when expanded in powers of μ is

$$f^2(0)=(p/\rho)(1+k/C_\infty-\mu\epsilon^2/C_\infty{}^2T^2) \tag{6''}$$

in agreement with (6). Similarly from (6) for ω very large

$$f^2(\infty)=(p/\rho)(1+k/C_\infty),$$

as is to be expected.

§3.

Case of three energy levels. The importance of an order of magnitude consideration in terms of the parameter μ becomes more evident when we consider transitions to two excited states for it is this factor which is instrumental in determining the choice of reactions to be considered. The reactions to be selected are of the type $N_i+N_j \rightleftarrows N_k+N_l$. Now the probability of such a reaction taking place is determined by two factors: (1) the probability of finding a molecule in state i and another in state j; (2) the probability that this pair of molecules have sufficient relative kinetic energy (plus vibrational energy) to effect the transition. Both these probabilities depend on the Boltzmann factor μ. With this in mind, we find beside the first order reaction (a) the following second order reactions to be considered:

$$\begin{aligned}
&\text{(b)} && N_0+N_0 \rightleftarrows N_1+N_1,\\
&\text{(c)} && N_0+N_1 \rightleftarrows N_1+N_1,\\
&\text{(d)} && N_0+N_1 \rightleftarrows N_0+N_2,\\
&\text{(e)} && N_0+N_0 \rightleftarrows N_0+N_2,\\
&\text{(f)} && N_0+N_2 \rightleftarrows N_1+N_1,
\end{aligned} \tag{8}$$

the last being a "resonance" reaction.[6]

Assuming the principle of detailed balancing for each of the six reactions (8) and (a) we can write two reaction equations for dn_1/dt and dn_2/dt analogous to (1), in which six independent reaction rate constants appear. Variation of these two reaction equations together with (4) modified by the additional term $(\epsilon_1+\epsilon_2)\Delta n_2$ yields three linear equations in Δn_1, Δn_2 and ΔT, from which $\Delta T/\Delta V$ may be found. ϵ_1 and ϵ_2 refer to the energy differences between the levels 0–1 and 1–2 respectively. The resulting expression for the velocity of sound is then of the form

$$f^2(\omega)=f_0{}^2+\mu f_1{}^2+\frac{p}{\rho}\frac{\alpha_0+\alpha_1\omega^2+\alpha_2\omega^4}{\beta_0+\beta_1\omega^2+\beta_2\omega^4+\beta_3\omega^6}\cdot\mu^2, \tag{9}$$

where $f_0{}^2+\mu f_1{}^2$ is just the expression (6). The α's and β's are rather involved combinations of T, ρ, ϵ_1, ϵ_2 and the reaction rate parameters which need not be given here.

The limit for large frequency remains, of course, unchanged. In the limit of small frequency (9) becomes just the expression (6''), with $\mu=\mu_1$, plus the second order term

$$(p/\rho)[\epsilon_1{}^4/kC_\infty{}^3T^4+(1/C_\infty{}^2T^2)\times(2\epsilon_1{}^2-(\epsilon_1+\epsilon_2)^2\mu_2/\mu_1)]\mu_1{}^2. \tag{9'}$$

Here $\mu_i=\exp(-\epsilon_i/kT)$. The result (9') agrees

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[5] The further transformations by which these authors introduce explicitly into (6) the C_i, see (7), are inconsistent with the above-mentioned order of magnitude considerations. Their result, however, when expanded is identical with (6) to terms of first order in μ.

[6] Richards has considered the reactions $N_i+N \rightleftarrows Nj+N$ where N is N_0, N_1, N_2 successively, $i=0, 1$, $j=1, 2$. Written out in detail these are

(a) $N_0+N_0 \rightleftarrows N_1+N_0$, (d) $N_1+N_0 \rightleftarrows N_2+N_0$,
(b) $N_0+N_1 \rightleftarrows N_1+N_1$, (e) $N_1+N_1 \rightleftarrows N_2+N_1$,
(c) $N_0+N_2 \rightleftarrows N_1+N_2$, (f) $N_1+N_2 \rightleftarrows N_2+N_2$,

so that one could expect to find in his results unwarranted contributions from (c), (e) and (f) while contributions from (8) (b), (e) and (f) will be absent. Reactions (c) and (e) are third order and (f) is a fourth order reaction. Richards has further assumed the reaction rate constants of each group of three reactions (a), (b), (c) and (d), (e) (f) to have separately a common value. This assumption seems doubtful; moreover a corresponding one does not seem possible in the case of reactions (8) and (a) due to the absence of symmetry in these as contrasted to the reactions of Richards. Therefore it appears necessary to introduce different rate constants for each reaction.

with the expansion in powers of μ of the expected result (6′) in which now

$$C_i=\frac{d}{dT}\frac{\epsilon_1\mu_1+(\epsilon_1+\epsilon_2)\mu_1\mu_2}{1+\mu_1+\mu_1\mu_2}.$$

Richards' result for this limiting case when expanded similarly, with $\mu_1=\mu_2$, is in accord with (9′). However this is to be expected since at low frequencies when the gas is in equilibrium, the particular reactions taking place can have no influence on the velocity of sound.

If we take all the κ's, except κ_f the resonance rate constant, to be of the order of the experimental value of κ_2, 3.67×10^{-14}, (Kneser), then for any reasonable value of κ_f the terms in (9) will decrease rapidly with higher powers of ω so that we may neglect all but the first term in the numerator and the first two terms of the denominator. The first and second order contributions may then be combined to give a frequency dependence for f^2 of the Kneser-Rutgers form with, however, another constant κ' replacing κ_2 of (6). We can then form an estimate of the second order effect by comparing κ' with κ_2. We find

$$\kappa'^2=\kappa_2^2(1-\gamma)/1-\gamma(\kappa_2^2/\kappa_f^2+2)$$
$$\gamma=\mu(\epsilon^2/kC_\infty T^2-2).$$

The center of the dispersion region (inflection point) is shifted by an amount

$$\Delta\omega=(\kappa'-\kappa_2)n/3\tfrac{1}{2}V.$$

Assuming for κ_f the extreme values $\kappa_f\sim1$, $\kappa_f\sim\kappa_2$ a numerical calculation for CO_2 at $T=300°$A yields for these two cases $\kappa'\sim3.85\times10^{-14}$ and 4.04×10^{-14}, respectively, corresponding to a shift $\Delta\omega\sim0.28\times10^5$ and 0.58×10^5 sec.$^{-1}$, and representing deviations of 5 and 10 percent. For intermediate values of κ_f, κ' and $\Delta\omega$ will assume intermediate values. The relative change of the velocity of sound in the dispersion region becomes of the order of present experimental accuracy so that at higher than room temperatures in CO_2 the second excited level should be considered.[7]

The author wishes to express his indebtedness and thanks to Professor G. E. Uhlenbeck for his advice and interest in the calculation.

[7] As Dr. Richards points out in the following note, which he so kindly permitted me to see before publication, there is in addition to the above considerations a further factor instrumental in determining the *a priori* probability of the reactions. Because of the finite mass ratios involved and the particular directional character required of the collision in order that excitation take place, the effectiveness of the translational-vibrational energy transfer will be decidedly limited. If we suppose that relative kinetic energy $\lambda\epsilon$ is necessary to excite vibrational energy ϵ, the probabilities of the six reactions (a) and (8) become of the order μ^λ, $\mu^{2\lambda}$, $\mu^{1+\lambda}$, $\mu^{1+\lambda}$, $\mu^{2\lambda}$, and μ^2 respectively. The parameter λ, which enters in the κ's implicitly, may be calculated from impulse considerations using the experimental value of κ_2. The result indicates that λ may easily be greater than 2, in which case the reactions (8) (b) and (e) may be justifiably omitted. This can be taken into account in the frequency dependent expression by setting the corresponding rate constants equal to zero. The α's and β's, however, are not sufficiently simplified to permit of their interpretation, the frequency dependence remaining as in (9), which, as pointed out in the text, is only approximately of the form (6). None of the numerical results given above will be affected appreciably. If we exclude all reactions involving excitation of more than one vibrational quantum, μ may still be used as a development parameter since the probability of second and third order reactions, for example, ($\sim\mu^{1+\lambda}$, $\mu^{2+\lambda}$, respectively) differ by a factor μ as before.

Comment on the Paper by M. E. Rose, Entitled "On the Dispersion of Sound. Consideration of Three Energy Levels"

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THERE can be no question that the ultimate second order theory of the dispersion of sound should be written only in terms of transition probabilities which are of the first and second orders, and Mr. Rose has found a compact and logical method for presenting this viewpoint. It is clear, therefore, that in a gas in which only the 0, 1 and 2 states need be considered collisions of the type N_2+N_2 will be so rare per second per unit volume that their effect on the rate of adjustment of the vibrational energy will be negligible in comparison with encounters of the type N_1+N_1. The appearance of third and fourth order reactions in my treatment of the second order theory is, as Mr. Rose has pointed out, illogical in this sense, but was required by the simplifying assumption that the collision of an N_i molecule with any other molecule of the same chemical composition having a given relative translational energy could be equally effective in bringing about the transition $N_i \rightarrow N_j$. This assumption was the only one I could find which gave a result of sufficient simplicity to permit its comparison with contemporary measurements. It would be surprising, however, if it were justified, and hence it is very probable that the expressions which I have given must ultimately be modified in order to describe the behavior of any actual gas.

I cannot agree with Mr. Rose, however, that the Boltzmann factor is alone sufficient to determine *a priori* the probability of a given transition. In all cases which have been investigated to date a considerable activation energy of collision has been found necessary for the conversion of vibrational into relative translational energy. There are, moreover, reasons of a theoretical character for believing that only a portion of the relative translational energy may become converted into vibrational energy on collision. When this is the case transitions of the type $N_0+N_0 \rightleftharpoons N_2+N_0$ become far less probable than those of the type $N_0+N_1 \rightarrow N_0+N_2$, although the order of probability of the two is the same according to Mr. Rose's criterion. Conversely the reaction $N_0+N_2 \rightleftharpoons N_1+N_1$ is more probable than any other "second order" process. The rate of this reaction can hardly be detected by acoustical measurements, however, since, in the ideal case of an harmonic oscillator, it involves no conversion of translational to vibrational energy, and, in any actual case, involves only a very small amount of conversion.

It appears at present that experiment may adequately be described, at least in many cases, by very simple expressions. If, as has been found with carbon disulfide and ethylene, groups of states corresponding to several vibrational modes leave the acoustical cycle with a common characteristic transition frequency, the original treatment given by Einstein may be retained almost without alteration. Reactions of the type $N_0+N_2 \rightleftharpoons N_1+N_1$ may materially assist in redistributing the vibrational energy, but this may be obtained from the rotational-translational energy by a single outstandingly efficient collision process. It will then be only the identification of the rate-determining process by acoustical means which presents serious difficulties.

The Raman Spectra of Some Compounds Containing Carbon-Bromine Bonds. Possible Changes of the Vibration Frequencies in Ionic Solutions

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Raman spectra of methyl bromoacetate and methyl phenylbromoacetate are reported. The carbon-bromine bond line of the former is similar to that for ethyl bromide, while in the latter it does not appear in its normal position at all. The spectra of methyl alcohol and ethyl bromide have been accurately redetermined; some minor additions result. Shifts of the methyl bromoacetate and methyl alcohol lines in solutions of bromides are found.

KINETIC data suggest that in certain chemical systems at least a portion of the reacting molecules are associated. Association should affect the Raman spectra, either producing new lines or shifting old ones. An attempt to obtain such evidence of complex formation in reactions of the Finkelstein type, whose mechanisms have been discussed by Olson[1] and by Bergman, Polanyi and Szabo,[2] was made but the results were negative. However, as most of the compounds and solutions studied have not been previously observed, it is thought worth while to report the results.

EXPERIMENTAL

Spectra were observed with a prism spectrograph of dispersion 34 cm^{-1}/mm at 4358A and 54 cm^{-1}/mm at 5025A. Three Pyrex mercury arcs with appropriate reflectors served as the source of illumination. Use of saturated aqueous $NaNO_2$ or 4 percent *m*-dinitrobenzene in benzene as a filter restricted excitation to 4358 in most cases. The frequencies of all lines were obtained by linear interpolation between wave numbers of the nearest lines of an iron arc, photographed on the same plate. This procedure is liable to some error. Therefore the weak mercury lines appearing on the plates were measured in a manner identical to that used for the Raman lines, and a comparison with the known frequencies gave the desired correction. This correction ranged from 0 to 2 cm^{-1}. The error in the values listed depends upon the nature of the individual lines, but is probably less than 1 cm^{-1} for all definite lines.

ETHYL BROMIDE

Eastman Kodak Company's product was refractionated from P_2O_5. An exposure of 25 hours with slit 0.04 mm was made. The lines obtained were: 290.5 (4), 560.3 (10 *b*), 959.4 (2 *b*), 1062.8 (2), 1244.7 (2), 1252.9 (2 *b*), 1444.0 (2 *b*), 2867.2 (2), 2924.4 (4), 2969.2 (2 *bb* or *d*). Here *b*=broad, *d*=double. All these lines have been observed before[3] but the line at 1245 has been resolved into a doublet for the first time.

A 1 : 1 mole mixture of ethyl bromide and methyl alcohol showed only a superposition of the lines of the two components.

In a solution of anhydrous lithium bromide and ethyl bromide in methyl alcohol having the composition (mole fract.) LiBr 0.072, C_2H_5Br 0.301, CH_3OH 0.627, no new lines appeared and it was found that the 290, 560, 959, 1062, 1445 and 2924 lines of ethyl bromide were unshifted within the limits ± 1 cm^{-1}.

METHYL BROMOACETATE

The Raman spectrum of methyl bromoacetate is given in Table I. It has not been observed before.*

[1] Olson, J. Chem. Phys. **1**, 418 (1933).

[2] Bergman, Polanyi and Szabo, Zeits. f. physik. Chemie **B20**, 169 (1933).

[3] Cleeton and Dufford, Phys. Rev. **37**, 362 (1931); Dadieu and Kohlrausch, Monatshefte **55**, 70 (1930).

* *Added in proof:* The Raman spectrum of methyl bromoacetate has recently been published by Cheng (Hua-Chih Cheng, Zeits. f. physik. Chemie **B24**, 293 (1934)). The agreement with the values listed above is fairly good.

TABLE I. *$CH_2BrCOOCH_3$ liquid. Prepared from bromoacetic acid and methyl alcohol by the method of Lepercq.*[4]

Twice redistilled at 10–20 mm. Slit 0.07 mm. Exposure 48 hours.

205.8 (2)	845.9 (2)	1404.8 (2)
278.4 (2)	882.4 (3)	1421.0 (3)
301.9 (2)	909.9 (2)	1454.3 (5)
374.1 (4 *b* and band to 420)	1003.2 (4 *b*)	1395 to (1 band)
	1116.4 (2)	1465
550.3 (10 *b*)	1153.4 (2 *b*)	1739.7 (7) and band to 1762
670.2 (7)	1189.6 ? (3)	2845.9 (2)
710.5 (7)	1215.5 (2 *b*)	2956.9 (5)
766.5 (1 *b*)	1287.8 (4)	2965 to 3050 (2 band)

A solution of methyl bromoacetate and lithium bromide in methyl alcohol with the composition (mole fractions) LiBr 0.123, $CH_2BrCOOCH_3$ 0.215, CH_3OH 0.662 gave the following results. No new lines were observed. The lines 278, 374, 550, 710, 845, 882 and 1739 were unshifted within the limits ± 1 cm^{-1}, 670 increased by 2 cm^{-1}, 910 appeared to decrease 3.5, but as it is quite broad this is not certain.

METHYL PHENYLBROMOACETATE

The ester was prepared from phenylbromoacetic acid (melting point 81°–82°. Kindly furnished by Miss M. J. Young) and methyl alcohol in the presence of sulfuric acid. Exposures of 15 to 48 hours were made on methyl alcohol solutions with slit widths of 0.05 to 0.07 mm. The lines obtained, averages over four exposures, are given in Table II. *bd* = band.

TABLE II. *$C_6H_5CHBrCOOCH_3$ in CH_3OH.*

246.1 (1)	616.2 (3)	1003.3 (7)
272.1 (1)	675±15 (1 *bd*)	1156.3 (2 *b*)
292.7 (1)	707.8 (1 *b*)	1184.5 (3 *bb*)
371.1 (1)	782.1 (3)	1218.3 (4)
403.0 (½)	846.9 (2 *b*)	1602.4 (7)
486.5 (2)	898.5 (2)	3064.7 (3)
566±18 (2 *bd*)		

Notable in the spectrum of methyl phenylbromoacetate is the absence of the C-Br line from its usual position at 550, where it has been found for all other aliphatic bromo compounds.[5]

In view of the thorough investigation of vibration spectra of carbonyl compounds now being carried out by Kohlrausch and his coworkers no attempt had been made to interpret the spectra of methyl bromoacetate and methyl phenylbromoacetate, observed for the first time in this work.

METHYL ALCOHOL

Methyl alcohol, used as a solvent, was rather carefully investigated. The interpretation given its spectrum is shown in Table III together with the results of others. The alcohol used was a commercial product twice fractionated with retention of only the center third. No lines of the common impurities were observed. The values listed are means from three plates with a slit of 0.05 mm and exposures to 41 hours.

TABLE III. *CH_3OH.*

Observed	Kohlrausch in *Der Smekal-Raman Effekt*[6]	Wood and Collins[7]
1032.3 (6 *b*)	1034 (5)	1028 (10)
1062.7 ? (1)		
1109.8 (1 *b*)		1107 (2)
1166 (1 *b*)		
	1362 (0)	
1452.2 (4 *b*) and 1430 to 1490 band center = 1470	1462 (5 *b*)	1457 (10)
		2729 (1)
2834.4 (5 *b*)	2835 (6 *b*)	2831 (10)
2919 (2 side band)		
2943.7 (4 *b*)	2943 (5 *b*)	2942 (10)
2980 (2 side band)		
	3388±85 (band)	

In an exposure at low dispersion 1360 was positively identified. 1063 is doubtful as it may possibly have been 2834 excited by the 4047A mercury line. The unsymmetric band at 1460 has been rather arbitrarily interpreted as a combination of line and band.

TABLE IV. *Shifts of the CH_3OH lines.*

Solution	7 mol % LiBr	13 mol % HBr	24 mol % LiBr
Line			
1032.3	+0.1	−1.7	−3.8
2834.4	+2.1	−0.3	+4.3
2943.7	+1.9	+1.1	+7.1

[4] Lepercq, Bull. Soc. Chim. (3) **11**, 297 (1894).

[5] Dadieu, Pongratz and Kohlrausch, Monatshefte **61**, 409 (1932).

[6] Kohlrausch, *Der Smekal-Raman Effekt*, p. 309.

[7] Wood and Collins, Phys. Rev. **42**, 386 (1932).

The methyl alcohol lines were slightly displaced in concentrated LiBr and HBr solutions. The changes are shown in Table IV and agree in direction with those observed by Hibben[8] for $ZnCl_2$ solutions, and by Goubeau[9] for $LiClO_4$ solutions. The alterations of the methyl alcohol lines are roughly proportional to concentration. They indicate a weakening of the C−O bond (1032 line) and a strengthening of the C−H bond (2900 lines). LiBr and HBr form complexes with methyl alcohol[10, 11] and it is to be expected that the intermolecular forces involved will effect the binding forces. The weakening of the C−O bond is in accord with the important part played by the oxygen in compound formation.[12, 13]

In conclusion I wish to thank Professor A. R. Olson for suggesting this topic.

[8] Hibben, Proc. Nat. Acad. Sci. **18**, 523 (1932).
[9] Goubeau, Naturwiss. **21**, 468 (1933).
[10] Turner and Bissett, J. Chem. Soc. **105**, 1777 (1914).
[11] Maas and McIntosh, J. Am. Chem. Soc. **34**, 1284 (1912).
[12] McIntosh, J. Am. Chem. Soc. **28**, 588 (1906).
[13] Archibald and McIntosh, J. Chem. Soc. **85**, 919 (1904).

The Para-Ortho Hydrogen Conversion by the Hydrogen Iodide Reaction and by Iodine Atoms

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The rate of conversion of para to ortho hydrogen was determined in the presence of equilibrium concentrations of hydrogen iodide and iodine. From these data, velocity constants and collision efficiencies for the conversion by iodine atoms were calculated. The results are in agreement with a theoretical equation derived by Wigner.

ON the basis of experiment there is no evidence of any appreciable difference between the velocity constant of a reaction involving ortho hydrogen and that of the corresponding reaction involving the para modification. Therefore, in any reversible reaction involving hydrogen in which the hydrogen is not in equilibrium with respect to its two modifications, the para and ortho modifications are removed by the reaction in the proportion existing in the reacting mixture, while the hydrogen formed by the reverse reaction is composed of para and ortho hydrogen in the equilibrium ratio, which is 1 : 3 if the reaction is taking place at a temperature above 250°A. If the hydrogen present at the start of a reaction contains a fraction of para hydrogen larger than the equilibrium proportion of $\frac{1}{4}$, the rate at which the fraction of para hydrogen changes can be related to the velocities of the forward and reverse reactions.

A method for determining the velocity constants of a reaction at equilibrium is thus made possible, at least in principle. A reaction suitable for experiment must satisfy several conditions: the equilibrium concentration of hydrogen must be large enough to allow the withdrawal of samples for analyses; the reaction must proceed with a moderate velocity in a temperature range below 750°A, where a thermal reaction becomes important; and the conversion reaction must not be catalyzed directly by any component of the reacting mixture.

At the inception of this investigation the hydrogen iodide reaction seemed an excellent example which satisfied these conditions. Moreover, reliable data on the velocity constants of this reaction were available and a simple and reasonable mechanism had been proposed to explain these data.

When the results of the experiments here reported had been analyzed, it was found that the values of the velocity constants of the hydrogen iodide reaction which were obtained were so much larger than those which had been obtained by Bodenstein[1] that it was necessary to look for an additional conversion mechanism. Experiments showed that the hydrogen iodide and iodine molecules had no catalytic effect. It was known that hydrogen atoms could effect the conversion of para to ortho hydrogen, but the equilibrium concentrations of hydrogen atoms at the temperatures at which the experiments had been performed were far too small to account for the large velocity constants. Similarly, any possible catalytic effect of the walls of the reaction tubes was not large enough to account for the observed rate of conversion.

The iodine atoms, the only remaining component of the reacting mixture, were tentatively considered to be responsible for the catalysis. This consideration was greatly strengthened by the appearance of a series of papers which showed, both theoretically and experimentally, that paramagnetic solids, gases and solutions are effective in catalyzing the para-ortho hydrogen

[1] Bodenstein, Zeits. f. physik. Chemie **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1899).

conversion.[2] Since iodine atoms are paramagnetic, it seemed reasonable to ascribe to them the additional rate of conversion beyond that calculated from Bodenstein's data. The experimental results are consistent with this assumption.

With this assumption, it is necessary to consider a mechanism involving two processes in accounting for the observed rate of conversion of para to ortho hydrogen:

$$H_2{}^p + I_2 \rightarrow 2HI \rightarrow H_2{}^0 + I_2$$

and

$$H_2{}^p + I \rightarrow H_2{}^0 + I.$$

The rate at which para hydrogen is removed by both processes is

$$-d[H_2{}^p]/dt = (K_1/2)[H_2{}^p][I_2] + K_2[H_2{}^p][I]. \tag{1}$$

K_1 as used here is the velocity constant of the formation of hydrogen iodide:

$$d[HI]/dt = -2d[H_2]/dt.$$

The rate at which para hydrogen is formed is

$$d[H_2{}^p]/dt = (K_1'/8)[HI]^2 + K_2'[H_2{}^0][I]. \tag{2}$$

The factor $\frac{1}{8}$ appears in the first term of the right side of Eq. (2) because only $\frac{1}{4}$ of all the hydrogen molecules formed are of the para modification. The net rate at which para hydrogen is removed is

$$-d[H_2{}^p]/dt = (K_1/2)[H_2{}^p][I_2] - (K_1'/8)[HI]^2 + (K_2[H_2{}^p] - K_2'[H_2{}^0])[I]. \tag{3}$$

When this is divided by the total concentration of hydrogen, and the following relationships are introduced:

$$\frac{[HI]^2}{[H_2][I_2]} = \frac{K_1}{K_1'} \quad \text{and} \quad \frac{K_2'}{K_2 + K_2'} = \frac{1}{4}$$

(since $K_2 = 3K_2'$ above room temperature), then Eq. (3) becomes

$$-dN_p/dt = (K_1/2)[I_2](N_p - \tfrac{1}{4}) + 4K_2'(N_p - \tfrac{1}{4})[I], \tag{4}$$

in which N_p is the mol fraction of para hydrogen. When Eq. (4) is integrated, there is obtained

$$N_p = \tfrac{1}{4} + (N_{p_0} - \tfrac{1}{4}) \exp\{-((K_1/2)[I_2] + 4K_2'[I])t\}. \tag{5}$$

With N_p and t measured, N_{p_0} known from the temperature of the charcoal catalyst, K_1 obtained from Bodenstein's data, and $[I]$ calculated from $[I_2]$ by the use of the equilibrium constant of the reaction $I_2 \rightleftharpoons 2I$, this equation can be solved for K_2, the velocity constant for the para to ortho hydrogen conversion:

$$K_2 = -\frac{3}{4[I]}\left\{\frac{\ln(4N_p - 1)}{t} + \frac{K_1}{2}[I_2]\right\}. \tag{6}$$

At the highest temperature used an additional process, due to the equilibrium concentration of hydrogen atoms, is effective in converting para to ortho hydrogen:

$$H + H_2{}^p \rightarrow H + H_2{}^0; \quad -dN_p/dt = K_3(N_p - \tfrac{1}{4})[H].$$

The inclusion of this process leads to the integrated equation

$$N_p = \tfrac{1}{4} + (N_{p_0} - \tfrac{1}{4}) \exp\{-((K_1/2)[I_2] + 4K_2'[I] + K_3[H])t\}. \tag{7}$$

The values of $K_3[H]$ were determined from blank experiments in which 1 : 1 para-ortho hydrogen only was heated.

[2] Farkas and Sachsse, Zeits. f. physik. Chemie **B23**, 1 (1933). Wigner, ibid. 28 (1933). Taylor and Diamond, J. Am. Chem. Soc. **55**, 2613 (1933). Taylor and Eyring, Proc. Am. Phil. Soc. **72**, 255 (1933).

Experimental

Mixtures of equilibrium proportions of 1 : 1 para-ortho hydrogen, hydrogen iodide and iodine were sealed into Pyrex reaction tubes, heated at a constant temperature for a measured length of time, and then rapidly cooled. The hydrogen iodide and iodine were frozen out with liquid nitrogen, each tube was opened and the hydrogen was analyzed for its ortho-para composition in a thermal conductivity cell.

Commercial electrolytic hydrogen was purified by passing it through a heated palladium tube, *F* in Fig. 1. C.P. iodine was resublimed and stored over phosphorus pentoxide. To obtain dry hydrogen iodide, a colorless concentrated solution of hydrogen iodide was dropped on phosphorus pentoxide in an evacuated generator *I*, and the gas was passed through a phosphorus pentoxide trap.

The form of the thermal conductivity cell adopted was essentially that used by other investigators. The principal difference lay in the fact that the spreader for the heated wire was held by a glass rod attached at the top of the cell to the electrode seal. The resistance of the cell wire (a 0.01 mm Wollaston wire) was measured by a very sensitive Wheatstone bridge. The wires used had resistances in the range 80–115 ohms at operating temperature.

The furnace was of the resistance type, with a large heat capacity. An iron jacket surrounded the reaction tube. Because of its high thermal conductivity this metal lining made the temperature of the reaction zone of the furnace uniform to within 1°. The temperature was measured with a calibrated chromel-alumel thermocouple and a potentiometer. It was possible to hold the temperature constant to within 1°.

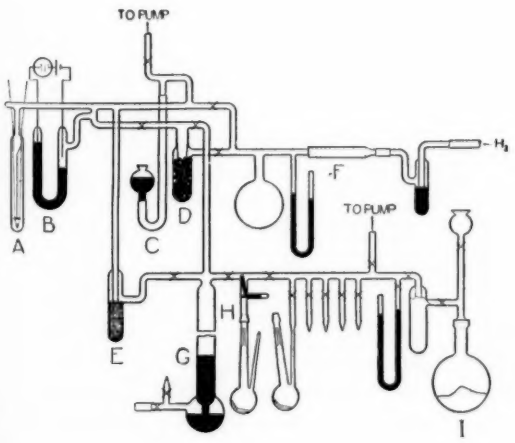

Fig. 1. Vacuum line. *A* is the thermal conductivity cell, *B* is a mercury manometer, *C* is a mercury piston, *D* is the activated charcoal catalyst, *E* is a trap, *F* is a palladium tube, *G* is a Toepler pump, *H* is an interchangeable ground glass joint and *I* is the hydrogen iodide generator.

The form and dimensions of the reaction tubes were chosen to give a volume large enough for duplicate analyses of the hydrogen, together with a small length to insure uniformity of temperature throughout the tube. A vacuum-tight connection was made between each of the reaction tubes and the vacuum line by means of an interchangeable ground joint *H*. The neck of each tube was closed off by a thin glass bubble which could be broken by releasing a weight with a small solenoid. A piece of capillary tubing in the side arm which was used to fill each reaction tube made negligible the effect of diffusion to the heated area when the tubes were sealed off.

The calculated equilibrium amounts of iodine were contained in capsules with capillary tips. To prepare one of these capsules an open capillary tip was drawn on a piece of 2 mm tubing. After this piece of tubing was weighed, an approximate amount of iodine was introduced into it and it was purged thoroughly with dry hydrogen while the capillary was kept in contact with solid carbon dioxide to prevent excessive loss of iodine. With the hydrogen flowing, the capillary and the other end of the capsule were successively sealed a few centimeters from the iodine. The capsule was weighed together with the rest of the original piece of tubing, and the weight of the iodine was obtained by difference. A capsule was sealed into each reaction tube (except those used for blanks); the tubes were sealed on the line and were evacuated to a pressure of 10^{-4} mm or lower.

A 1 : 1 para-ortho hydrogen mixture was obtained by placing liquid nitrogen around the tube *D* which contained degassed activated charcoal, and allowing the charcoal to adsorb hydrogen until the pressure above the charcoal was about 20 cm. After an interval of an hour, some of the hydrogen was pumped away; then the reaction tubes were filled to a desired pressure

of 1 : 1 para-ortho hydrogen by means of the Toepler pump G. The stopcocks on the tubes were closed, the hydrogen remaining in the line was pumped out, and hydrogen iodide was added to each tube until the desired total pressure was reached. An effort was made to have each stopcock attached to a reaction tube open for as short a time as possible to prevent diffusion of hydrogen. The reaction tubes were sealed off at a previously prepared constriction and the capillaries of the iodine capsules were broken by shaking the tubes. The tubes were then ready to be placed in the furnace.

After a tube was heated for a measured length of time, it was removed from the furnace and cooled as quickly as possible in the air current of an electric fan. The grind on the tube was fitted into the one on the line H and the line was evacuated while the reaction tube was immersed in liquid nitrogen to condense the iodine and hydrogen iodide. The breaker was released to open the tube and a sample of hydrogen was pumped with the Toepler pump into the thermal conductivity cell A through the trap E immersed in liquid nitrogen to prevent traces of iodine and hydrogen iodide from reaching the cell. The pressure of hydrogen in the cell was adjusted with a mercury piston to a value of approximately 40 mm, which was reproducible to 0.02 mm. The thermal conductivity cell was always covered with liquid nitrogen, the level of which was kept constant. After the current had been regulated, the resistance of the cell was measured.

Results

With the final composition of the hydrogen N_p determined this value could be substituted in Eq. (6), and since the other quantities were known, K_2 could be calculated. By using the average value of K_2 for each temperature, the mol fraction of para hydrogen could be recalculated and compared with the experimental value. The data obtained are compiled in Table I, from which the agreement between the calculated and observed values can be seen.

No changes were noticed in the blank experiments carried out at a temperature of 716°A or lower.

The errors in the pressures of hydrogen and hydrogen iodide were less than 0.5 percent. The volumes of the reaction tubes were measured to within 1 percent. The iodine was weighed by difference; the weighing error varied from 0.3 to 4 percent. An error in the concentration of iodine did not cause an equal error in the observed value of N_p, however, because of the logarithmic relationship between the iodine concentration and N_p and the fact that the equilibrium concentration of iodine is established during the heating period. The intense heat required to seal off the tubes caused a slight amount of conversion which was reduced to a negligible value by the use of capillary tubing in the side arm of the reaction tubes. The temperatures of the reaction tubes were within one degree of the reported temperatures.

A possible source of error is the catalytic effect of the Pyrex walls of the reaction tubes. H. A. Taylor[3] found a relatively small variation in the decomposition velocity constant with surface-volume ratio, using crushed glass to increase the

Table I.

I_2 (moles/cc) 10^7	Time (sec.)	N_p Calc.	N_p Obs.
	Temperature 753°A Mean constant 9960 cc/mol sec.		
2.54	7860	0.289	0.283
3.33	7500	.281	.292
1.95	5120	.340	.326
1.14	4380	.383	.392
1.88	5280	.339	.351
2.84	4500	.329	.326
3.84	6500	.284	.284
0.91	5480	.376	.368
Blank	7200		.466
Blank	7200		.446
Blank	7200		.462
	Temperature 716°A Mean constant 3690 cc/mol sec.		
4.27	7020	0.407	0.417
6.92	7220	.377	.375
10.3	7770	.343	.348
6.18	8080	.374	.376
7.60	9200	.348	.343
10.4	7730	.343	.348
6.12	9800	.358	.358
4.79	6260	.409	.407
10.3	7770	.343	.348
	Temperature 693°A Mean constant 2600 cc/mol sec.		
6.20	9660	0.424	0.426
7.34	13610	.391	.402
6.94	5770	.448	.439
7.46	8030	.428	.429

[3] H. A. Taylor, J. Phys. Chem. **28**, 984 (1924).

surface. In the present work, however, the surface-volume ratio was smaller than any in Taylor's work, approximately 1.4 cm^{-1}, and the walls were smooth. That the condition of the wall had no marked effect on the reaction velocity was shown by a comparison between reaction tubes which had not been cleaned carefully and those which had been cleaned with hot $K_2Cr_2O_7-H_2SO_4$ solution just before sealing off.

Discussion

It can be seen that the use of the mean velocity constant leads to calculated values of N_p which are in agreement with the data. The consistency of the data can also be judged from the deviation from the mean of the individual values of the velocity constant which is less than 15 percent with the exception of two values, one of which deviates by 30 percent, the other by 25 percent. In view of the fact that each determination involves a considerable number of manipulations and that the desired constant is obtained as a difference, this degree of concordance is as high as could be expected.

From the values of the velocity constants, the collision efficiency can be calculated for each temperature. In particular, the collision efficiency for the para to ortho hydrogen conversion can be obtained by dividing the product of the corresponding velocity constant, the concentration of para hydrogen molecules and the concentration of iodine atoms by the total number of collisions between para hydrogen molecules and iodine atoms. The calculation of this total number of collisions depends on an assumed value for the closest distance of approach between a hydrogen molecule and an iodine atom, since this quantity has not been determined. With an assumed distance of approach of 2A, the collision efficiency for the para to ortho hydrogen conversion is found to be 9.4×10^{-12}, 13×10^{-12} and 34×10^{-12} at 693, 716 and 753°A, respectively.

It is of interest to compare these values with some obtained from a theoretical equation of Wigner[4] and with experimental data obtained by Farkas and Sachsse[4] for other reactions. By an application of quantum mechanics, Wigner has derived expressions for the probability of a para to ortho conversion in those collisions in which the required energy is present:

$$P_{j\to j+1}=1.1\times10^{-17}\frac{\mu^2}{a^6T}\frac{j+1}{2j+1}$$

$$P_{j\to j-1}=1.1\times10^{-17}\frac{\mu^2}{a^6T}\frac{j}{2j+1}$$

in which μ is the magnetic moment of the paramagnetic particle (in this case the iodine atom), a is the effective minimum distance of approach, T is the absolute temperature, j is the rotational quantum number of the hydrogen molecule, and the factor 1.1×10^{-17} contains only universal constants and the square of the magnetic moment of the proton.

The normal state of the iodine atom is $^2P_{3/2}$. Its magnetic moment, calculated from the expression $\mu=[g^2j(j+1)]^{\frac{1}{2}}$ (g, the Lande splitting factor) is 2.58 Bohr units or 2.38×10^{-20} gauss cm. It is unnecessary here to consider any excited state of the iodine atom, since the fraction of atoms in the first excited state, $^2P_{1/2}$, is only 3×10^{-7} at 750°A.

In the complete absence of any information about the quantity a, we may assume, with Farkas and Sachsse, a value of 1A. It should be observed that this distance need not coincide with the kinetic theory distance of closest approach, usually obtained from viscosity data, which was used to calculate collision efficiencies from experimental data.

When these values are introduced into Wigner's expressions and the effective value of the factor involving j is obtained by summing over five[5] rotational states of the hydrogen molecule, the probability, and thus the collision efficiency, of para to ortho transitions is found to be 6.2×10^{-12}, 6.0×10^{-12} and 5.8×10^{-12} at 693, 716 and 753°A, respectively.

It is evident that so far as the order of magnitude of the collision efficiency is concerned, the theory is in agreement with the experimental data. However, the theoretical equation of Wigner requires a very small negative temperature coefficient, while the temperature coefficient of collision efficiency obtained experimentally has a small positive value. It is not surprising that the

[4] See reference 2.

[5] The fraction of molecules with a j value of 5 is only 0.035.

agreement is less good at the higher temperatures since the theory was designed to fit a lower temperature range.

The results of Farkas and Sachsse for a number of paramagnetic substances are also in agreement with Wigner's equation. In particular, the order of magnitude they obtained for the collision efficiency of NO(2×10^{-12}) is approximately the same as that found in the present work with iodine atoms. They, too, found a positive temperature coefficient in the temperature range 600–750°A.

It might be worth while to mention at this point a confirmation of a result obtained by a previous investigator. A. Farkas,[6] in the study of the thermal conversion of para to ortho hydrogen, determined values for the velocity constant for this reaction which have a small temperature coefficient and from which the extrapolated value at 750°A is approximately 9×10^{11} cc/mol sec. From the blank experiments at 753°A, $K_3[H]=2.6\times10^{-5}$. The hydrogen atom concentration at this temperature calculated from the equilibrium constant is 2.3×10^{-17} mols/cc. From these data the value of K_3 is

$$(2.6\times10^{-5})/(2.3\times10^{-17})=11\times10^{11}$$

which confirms the values obtained by Farkas.

[6] A. Farkas, Zeits. f. physik. Chemie **B10**, 419 (1930).

On the Activation Energy of Unimolecular Reactions[1]

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(Received February 23, 1934)

By using the principle of microscopic reversibility, unimolecular decompositions are considered from the point of view of the reverse reaction, which is a bimolecular association. In cases where the immediate product of the decomposition is a pair of free radicals, it is assumed that the probability of these free radicals recombining upon collision is independent of their energy. An explicit expression for the activation energy in terms of the energy of reaction and the thermal properties of the molecules involved is thus obtained. From this one may calculate the energy of activation at absolute zero and the energy necessary to break the bond which falls apart in the reaction, quantities which may differ considerably from each other and from the energy of activation at the temperature of reaction. The results are applied to several cases of interest, and are critically compared with those of the earlier theories of Rice and Ramsperger, Kassel and Rice. A brief discussion is given of the calculation of the rate constant as a function of pressure, and its modification according to the point of view of the present paper.

I. INTRODUCTION

OF the theories that have been put forth to explain the experimental data on homogeneous first order gas reactions, those that give best agreement with the data are theory II of Rice and Ramsperger, the classical and quantum theories of Kassel and the quantum theory of Rice.[3] All these involve arbitrary assumptions about the nature and mechanism of dissociation. It is assumed that a necessary (but not sufficient) condition for reaction is that the total energy of the molecule be equal to or greater than a constant quantity ϵ_0. A second necessary condition is that this energy be localized in the molecule. According to the theory of Kassel, the energy must be localized in a bond (two energy terms), that is, the bond that breaks. This permits an identification of ϵ_0 with the energy of the bond.[4] It can be shown that the translational energy of the molecule does not contribute to the energy necessary for dissociation, while usually rotational energy contributes a trivial amount, so that only those molecules that have vibrational energy greater than or equal to ϵ_0 can react. Sometimes, to get agreement with experiment, it is necessary to assume that only a few of the vibrational degrees of freedom take part.

A consequence of the classical theories of Rice and Ramsperger and of Kassel, and of the quantum theory of Kassel, as well, is that for high pressures the energy of activation, as determined by the temperature coefficient of the rate constant, is equal (or at least very approximately equal) to ϵ_0; and it has been more or less customary to consider that the energy of activation gives an experimental determination of ϵ_0. According to the quantum theory of Rice, however, ϵ_0 may be very considerably less than the energy of activation, and hitherto there has been no satisfactory way of determining which of the quantum theories gives the most nearly correct extension of the classical theories.[5]

The difference between the theories is due to different arbitrary assumptions made in calculating the probability that in a molecule having energy $\epsilon > \epsilon_0$, ϵ_0 or more will be localized in a given part of the molecule. It would, therefore,

[1] Presented, in part, at the Boston meeting of the American Association for the Advancement of Science, December, 1933.

[2] Thayer Fellow.

[3] (a) O. K. Rice and Ramsperger, J. Am. Chem. Soc. **40**, 1617 (1928). (b) Kassel, J. Phys. Chem. **32**, 225, 1065 (1928). (c) O. K. Rice, Proc. Nat. Acad. Sci. **14**, 114, 118 (1928). For a more detailed analysis of these theories than will be given in this paper and for a more complete list of references to original papers, see (d) Kassel, *Kinetics of Homogeneous Gas Reactions*, Chem. Cat. Co., 1932, especially Chapter V.

[4] More exact definition of the various energy quantities will be given below.

[5] O. K. Rice, *L'Activation et la Structure des Molecules*, Réunion Internationale de Chimie Physique, Paris, 1928, p. 309. Kassel, reference 3 (d), pp. 105–6.

be of great advantage if we could replace these assumptions by some of a more rational character. We believe that we have been able to do this by making use of the principle of microscopic reversibility and considering the reverse reaction, for decompositions in which the reverse reaction has no activation energy or in which the activation energy of the reverse reaction consists only of the mutual translational energy of the recombining parts; and on the basis of more careful definitions of the various quantities involved we have considered the calculation of the energy of the bond and the energy of activation at absolute zero from the observed activation energy.

Recently, with a different goal in view, Rodebush[6] has given a quasithermodynamic derivation of the rate of reaction for a simple type of unimolecular reaction by a somewhat similar use of the reverse reaction. In this paper we shall go more deeply into the statistics involved in the treatment of the direct and reverse reactions, and shall at first restrict our discussion to the energy of activation at high pressures, where the Maxwell-Boltzmann distribution is maintained.

II. General Considerations

According to the principle of microscopic reversibility the reaction in equilibrium with a unimolecular decomposition is a bimolecular association.[7] Let us consider the reaction $AB \rightleftarrows A+B$. At equilibrium the number of molecules AB that are dissociating is equal to the number of molecules AB that are being formed by the bimolecular association of A and B. Furthermore, the average energy of the molecules AB that are dissociating is equal to the average energy of those being formed. Therefore we have the relation

$$\hat{\epsilon}_{AB}+\epsilon_{AB}^{\circ}=\hat{\epsilon}_{A}+\epsilon_{A}^{\circ}+\hat{\epsilon}_{B}+\epsilon_{B}^{\circ}+\mathfrak{E} \qquad (1)$$

where $\hat{\epsilon}_{AB}+\epsilon_{AB}^{\circ}$, $\hat{\epsilon}_{A}+\epsilon_{A}^{\circ}$, and $\hat{\epsilon}_{B}+\epsilon_{B}^{\circ}$ are respectively the average energies of the molecules of AB, A and B that actually react,[8] and $\mathfrak{E}$ is the energy of the bond that is formed.[9] The quantities ϵ_{AB}°, ϵ_{A}° and ϵ_{B}° are the respective zero point vibrational energies, while the other symbol designates the average energy of those molecules which *react*, in excess of the zero point energy.

We wish now to consider the activation energy of the direct and reverse reactions. Activation energy has been defined in many ways by previous investigators.[10] For cases in which the Maxwell-Boltzmann quota of activated molecules is maintained, i.e., the cases in which equilibrium statistics can be applied, the most rigorous definition of activation energy is that given by Tolman,[8] as the difference between the average energy of the molecules that react and the average energy of all the molecules. Therefore for the activation energy of a unimolecular reaction we have

$$\epsilon_a=\hat{\epsilon}_{AB}-\bar{\epsilon}_{AB}, \qquad (2)$$

where $\bar{\epsilon}_{AB}$ is the average energy of all the

[6] Rodebush, J. Chem. Phys. **1**, 440 (1933). La Mer (J. Chem. Phys. **1**, 289 (1933)) has also considered energy of activation as a function of temperature but has applied his results only to reactions in solution.

[7] The possibility of bimolecular association has been discussed by Kassel, J. Am. Chem. Soc. **53**, 2143 (1931).

[8] See Tolman, *Statistical Mechanics*, pp. 261–2, Chem. Cat. Co., 1927. Our definitions of $\hat{\epsilon}_{AB}$, $\hat{\epsilon}_{A}$, and $\hat{\epsilon}_{B}$ are the same as Tolman's definition of the corresponding quantities.* But see reference 11.

All average energies include the translational energy.

* In previous published work the symbol ϵ with two bars above it has been used for this quantity. Throughout this paper the symbol $\hat{\epsilon}$ is being substituted.

[9] The exact significance of the quantity $\mathfrak{E}$ is perhaps best understood by considering the corresponding quantity for diatomic molecules, namely, the energy from the minimum of the lowest potential energy curve representing the bond to its asymptote (if potential energy curves cross, to the lowest asymptote). It is therefore identical with the quantity that spectroscopists call D_e (Jevons, *Report on Band Spectra*, Chap. IX, Cambridge University Press, 1932). It must be distinguished from D_0, the quantity that is experimentally determined spectroscopically, and which differs from it by the amount of the zero point energy. In this paper we shall call $\mathfrak{E}$ the energy of the bond, and distinguish it from ΔE_0, the energy change of the reaction at absolute zero, which gives the difference between the energy of the associated molecule in its lowest energy state and the energy of the dissociated particles in their lowest energy states. The difference between $\mathfrak{E}$ and ΔE_0 will be given by the difference between the zero point energy of the associated molecule and the sum of the zero point energies of the dissociated particles. In the literature the concept of bonding energy for the case of polyatomic molecules has not been unequivocally defined.

[10] See for example Rice and Ramsperger, J. Am. Chem. Soc. **49**, 1618 (1927); and Kassel, reference 3 (d), p. 21.

molecules AB in excess of their zero point energy. Similarly, for the bimolecular reaction the activation energy will be given by[11]

$$\epsilon_a' = \mathring{\epsilon}_A + \mathring{\epsilon}_B - \bar{\epsilon}_A - \bar{\epsilon}_B. \quad (3)$$

Combining Eqs. (1), (2) and (3),

$$\epsilon_a = \bar{\epsilon}_A + \bar{\epsilon}_B - \bar{\epsilon}_{AB} + \epsilon_a' + (\mathfrak{E} + \epsilon_A^\circ + \epsilon_B^\circ - \epsilon_{AB}^\circ). \quad (4)$$

If now we let ΔE be the energy of reaction and ΔE_0 the energy of reaction at absolute zero,[12] then according to the usual definitions of these quantities

$$\epsilon_a = \bar{\epsilon}_A + \bar{\epsilon}_B - \bar{\epsilon}_{AB} + \epsilon_a' + \Delta E_0, \quad (5a)$$

$$\epsilon_a = \epsilon_a' + \Delta E. \quad (5b)$$

We shall need a special symbol for the activation energies of the unimolecular and bimolecular reactions at absolute zero; they will be denoted respectively by $\epsilon_{a,\,0}$ and $\epsilon'_{a,\,0}$.

In many recombinations that involve heavy free radicals it seems very probable that no activation energy will be required (we neglect the "energy of activation of collision"[11]). This is the case that will be considered first. For this special case Eq. (5b) reduces to

$$\epsilon_a = \Delta E \quad (6a)$$

and we also have

$$\epsilon_{a,\,0} = \Delta E_0. \quad (6b)$$

The equations of this section are not new in themselves,[13] but the terms which enter into them do not seem to have been carefully defined; when this is done their range of applicability is much increased.

III. Discussion of the Activation Energy in Several Special Cases

The derivation of Eqs. (6a) and (6b) is almost on a thermodynamic basis. Nevertheless, it may not be entirely superfluous to mention several cases in which it may be shown that they are substantiated by the experimental facts.

An example in which (6b) is applicable is afforded by measurements recently made in this laboratory by Dr. R. A. Ogg, Jr., on the unimolecular decomposition of methyl iodide into methyl radicals and iodine atoms.[14] The experimentally determined activation energy is equal to ΔE_0 for the C – I bond as calculated from thermochemical data. In this case the change of the vibrational energy (indeed, the whole vibrational energy) will be negligible.

All the information necessary to test (5b) is supplied by data available on the reaction $C_2H_6 \rightleftarrows C_2H_4 + H_2$. The decomposition of ethane has been studied by Marek and McCluer[15] who find it to be a first order reaction with an activation energy of 73.0 kg cal. per mole. The association has been studied by Pease[16] and

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[11] In the case of the bimolecular reaction our definition differs slightly from that of Tolman. He defines the energy of activation as the average energy of all pairs of reacting molecules minus the average energy of all pairs of *colliding* molecules. This is not very clearly brought out in his book, but is clearly stated by Kassel, reference 3 (d), p. 26. We define the activation energy as the average energy of all pairs of reacting molecules minus the average energy of *all* pairs of molecules. The latter quantity is $\frac{1}{2}kT$ less than the average energy of the colliding pairs (i.e. we have an "energy of activation of collision"), so that in this way we avoid the term $\frac{1}{2}T$ which appears in Tolman's Eq. (614). If we write N_A, N_B, and N_{AB} for the concentrations of the respective molecules and define K' by the equation $dN_{AB}/dt = K'N_AN_B$, where dN_{AB}/dt represents the rate of increase of N_{AB} due to reaction between A and B, we have simply

$$kT^2 d \log K'/dT = \mathring{\epsilon}_A + \mathring{\epsilon}_B - \bar{\epsilon}_A - \bar{\epsilon}_B.$$

If we combine this with the equation

$$kT^2 d \log K/dT = \mathring{\epsilon}_{AB} - \bar{\epsilon}_{AB}$$

for the unimolecular reaction, it is readily seen from the immediately following development of this paper that we get the correction thermodynamic relation for the temperature dependence of the equilibrium constant K'/K. It must be noted, however, that if the bimolecular rate constants are defined in terms of partial pressures rather than concentrations a slight correction must be made. Such a correction has in fact been applied in the case of the data on the association of ethylene and hydrogen discussed below.

[12] For thermodynamic quantities we use the notation of Lewis and Randall, *Thermodynamics* (McGraw-Hill, 1923).

[13] For example, they have been used by Bodenstein and Jung (Zeits. f. physik. Chemie **121**, 129 (1926)), who got them from Trautz (Lehrbuch d. Chemie **1**, 406 (1922); **3**, 81 (1926), Berlin). The relation used here was not exact being $Q = \epsilon_a - \epsilon_a'$ where Q is the *heat of reaction*.

[14] R. A. Ogg, Jr., J. Am. Chem. Soc. **56**, 526 (1934).

[15] Marek and McCluer, Ind. Eng. Chem. **23**, 878 (1931).

[16] Pease, J. Am. Chem. Soc. **54**, 1876 (1932). We have made our calculations for Pease' temperature, about 800°K. Marek and McCluer worked at slightly higher temperatures, but this difference can be neglected.

found to be bimolecular with an activation energy of 44.75 kg cal. per mole. (This has been corrected so that it applies to the rate constant expressed in terms of concentrations rather than pressures.[11]) The heat of hydrogenation at room temperature (ΔH_{300}) has been determined by v. Wartenburg and Krause[17] as 30.6 kg cal. per mole. ΔC_p as a function of temperature is given by the equation $6.5-0.004T$ cal. per mole per degree.[18] If we make the approximation $\Delta C_v = \Delta C_p - R$ we may replace ΔE by $\Delta H - RT$. We have therefore

$$\epsilon_{a,\,800} = \Delta H_{800} - RT + \epsilon'_{a,\,800}$$

$$= \Delta H_{300} + \int_{300}^{800} \Delta C_p dT - R \cdot 800 + \epsilon'_{a,\,800}.$$

$$= 76.0 \text{ kg cal. per mole,}$$

the subscripts denoting the absolute temperatures at which the quantities are evaluated. This compares favorably with Marek and McCluer's value of 73.0 kg cal.

Pease has already made a calculation to show that the ratio of the reverse and direct reaction rates gives the equilibrium constant, which involves essentially the above calculation, except that it does not take account of the ΔC_v term. This term is small in this case, involving as it does only small molecules. Since (5b) differs from equations in common use only in that these terms involving the vibrational and other internal energy are explicitly taken into account, it would be of more interest if it could be verified for a case in which these are large, but data for this purpose are not available.

The real importance of the equations of Section II lies in the fact that they give us the possibility of calculating $\mathfrak{E}$ and $\epsilon_{a,\,0}$ in various cases and comparing with the quantum theories of Kassel and Rice. This comparison is, however, rendered difficult by the fact that the zero point energy was not carefully considered in the earlier work. It was treated as a more or less non-distributable and constant residue of energy. On this basis it would seem that the quantity called E_0 by Kassel[3b] and ϵ_0 by Rice[3c] corresponds more nearly to our $\epsilon_{a,\,0}$ than to our $\mathfrak{E}$. Accepting this identification, then according to the theory of Kassel $\epsilon_{a,\,0}$ should always be just equal to the activation energy at the temperature at which it is measured, while according to the theory of Rice it should be less than the energy of activation at the temperature of reaction and increasingly so for larger molecules. We may thus consider $\epsilon_{a,\,0}$ in attempting to form an opinion as to which of the older theories is the better approximation, but $\mathfrak{E}$ would seem to be intrinsically the more interesting quantity, and we shall consider how to calculate both of them from ϵ_a.

The calculation of $\epsilon_{a,\,0}$ and $\mathfrak{E}$ rests upon our ability to find out something about the reverse reaction. In cases where dissociation is into free radicals it seems reasonable to assume that the bimolecular association requires no activation energy,[19] which implies that the steric factor is essentially independent of the energy. This very important assumption will be shown in the next section to take the place of the assumption made in the previous theories of unimolecular decomposition that the rate of reaction of a molecule of a given energy is proportional to the fraction of such molecules which at equilibrium would have sufficient energy localized in a given bond. This latter assumption was purely *ad hoc;* the one which replaces it seems very natural, especially if a large number of degrees of freedom are involved in the reaction; for at the energy at which a molecule is activated the energy levels are fairly closely and uniformly spaced in an actual molecule.[20] The probability of two

[17] v. Wartenburg and Krause, Zeits. f. physik. Chemie **151**, 105 (1930).

[18] Parks and Huffman, *The Free Energies of Some Organic Compounds*, p. 80, Chem. Cat. Co., 1932.

[19] A consideration of this assumption, and how our results would be affected if it does not hold, will be given later on in the paper. We should remark that there is some evidence that free methyl radicals do not combine in the gas phase (Ogg, reference 14; Bates and Spence, J. Am. Chem. Soc. **53**, 1689 (1931)). Since the recombination does not occur over a considerable temperature range it is unlikely that need of activation energy is the cause but rather some quantum-mechanical selection rule concerning rotation. Work is now being done on this problem.

[20] To verify this point the spectrum of the vibrational energy levels of the cyanogen molecule was plotted as far as the level representing 27.43 kg cal. per mole. Between 26.01 kg cal. and 27.43 kg cal. there are ten separate energy levels. As the total energy of the molecule increases the

radicals recombining also depends upon the amount the energy level, into which they are to go, is broadened. But all the energy levels are presumably equally broadened, since the broadening depends upon the lifetime of the molecule in the given state, and the latter quantity depends only upon the collision frequency, when the pressure is sufficiently high.

In order to see how our assumption works out it is desirable to treat a specific case which is as simple and exact as possible. To avoid arbitrary assignation of vibrational frequencies an actual molecule with known frequencies is preferable. For this purpose the cyanogen molecule was chosen. Although there are no data on the kinetics of the reaction, the equilibrium $C_2N_2 \rightleftarrows 2CN$ had been studied by G. B. Kistiakowsky and one of us,[21] and the vibrational frequencies are known. Hence it is possible to assume that the decomposition is unimolecular, and to calculate $\epsilon_{a,0}$ and $\mathfrak{E}$ in terms of ϵ_a. Since we assume $\epsilon_a' = 0$, it follows that the average energy of the radicals that combine upon collision is equal to the average energy of all the radicals. We can, therefore, set up our equilibrium statistics and calculate the energy distribution at equilibrium.

The molecules CN and C_2N_2 each have, of course, three translational degrees of freedom, and since the molecules are linear they have only two degrees of rotational freedom. CN radicals have one vibrational frequency, while C_2N_2 has seven normal modes of vibration, only five of which are distinct, as due to the symmetry of the molecule the transverse vibrations are double. We thus get, for the average energies of CN and C_2N_2, respectively,

$$\bar{\epsilon}_{CN} = (5/2)kT + h\nu_0/[\exp(h\nu_0/kT) - 1] \quad (7)$$

where ν_0 is the vibration frequency of CN, and

$$\bar{\epsilon}_{C_2N_2} = (5/2)kT + \sum_{i=1}^{i=7} h\nu_i/[\exp(h\nu_i/kT) - 1] \quad (8)$$

where the ν_i are the vibrational frequencies of C_2N_2. If we now insert the necessary numerical values of the vibrational frequencies[22] and let $T = 1500°K$, the temperature at which the equilibrium was studied, we obtain

$$\bar{\epsilon}_{CN} = 8.47 \text{ kg cal. per mole} \quad (9a)$$

$$\bar{\epsilon}_{C_2N_2} = 19.87 \text{ kg cal. per mole.} \quad (9b)$$

Hence

$$\epsilon_{a,0} = \Delta E_0 = \epsilon_a + 2.9 \text{ kg cal. per mole.} \quad (10)$$

The zero point energy of cyanogen is 11.2 kg cal. per mole (being $1/2\ h\nu$ for each oscillator) and that of cyanide radicals 2.9 kg cal./mole, so using Eqs. (4) and (10), we get

$$\mathfrak{E} = \epsilon_a + 8.3 \text{ kg cal. per mole.} \quad (11)$$

Considering the high temperature involved it is seen that the effect of the internal energy is not large in this case which deals with a rather small molecule, though the difference between $\mathfrak{E}$ and ϵ_a is nevertheless appreciable. For molecules of this small size neither the theory of Rice nor that of Kassel would demand much difference between $\epsilon_{a,0}$ and ϵ_a. Since, however, such deviation as exists is in the opposite direction to that predicted by the theory of Rice it would appear that as far as may be indicated by this specific case the theory of Kassel is to be favored.

Before considering the application of the equations of Section II to more complicated molecules it is desirable to examine more closely the relation between the concepts of "binding energy" and energy of dissociation of organic compounds as used in the literature. The calculations of Pauling[23] have shown that to each bond in an organic compound can be assigned an energy practically independent of the compound, such that the sum of all the "binding energies" gives the energy of formation of the compound from its component atoms. In the application of these binding energies to chemical data it has been assumed (at least implicitly) that they should be equal to the energy of breaking the molecule into two parts at that bond. Thus in order to explain the low dissociation energies of the highly substituted ethanes it has been necessary to assume that the bond is weakened, in the cases where phenyl groups are the substituents by resonance,[24] and in others by steric hindrance; more careful investigation, however, indicates that there is no reason

energy levels become closer together. Since the energy of dissociation for this molecule is about 77 kg cal. the energy levels in this region will be exceedingly close together. See also, Kassel, reference 7.

[21] Kistiakowsky and Gershinowitz, J. Chem. Phys. **1**, 432 (1932).

[22] Reference 21, p. 436.

[23] Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

[24] Pauling and Wheland, J. Chem. Phys. **1**, 362 (1933).

to expect the dissociation energy to be equal to the bonding energy. The quantity measured in chemical reactions is ΔE_0, the difference between energies of the products and the reactant, both with their zero point energies. Even though the energy of all the carbon-carbon bonds in heptane were the same we should expect that at absolute zero the energy required to break off an end CH_3 group would be different from that required to break the chain in the middle, simply because the products have different zero point energies in each case. In calculating energies of formation, however, the zero point energy is of a so much smaller magnitude than the total energy of formation that it can be neglected. But when we consider ordinary chemical decompositions, involving only one bond and try to compare the energy of dissociation with a so-called "binding energy" it is first necessary to investigate the ΔC_v change in the reaction, as well as the change in zero point energy.

Thus there are two distinct quantities that have been called binding energy in the literature, one of which corresponds to our ΔE_0, the other to $\mathfrak{E}$. The quantity calculated by quantum mechanics,[25] at least for diatomic molecules, is $\mathfrak{E}$. This, therefore, is the quantity that might be expected to be constant for a given bond in various compounds if anything is. On the whole, however, there is little evidence either experimental or theoretical for the constancy of either quantity. Quantum-mechanical calculations by Eyring[26] show in fact that the hydrogens on ethane are bound less firmly than those on methane. A wave-mechanical analysis of methane using group theory indicates that it takes more energy to pull off the first hydrogen than the rest.[27] Heitler and Schuchowitzki,[28] investigating bonding energy in organic molecules, find no way of explaining why it should be constant to more than 20 percent at best. As we have stated above, these binding energies are not the same as those considered by Pauling.[23] The equations derived in this paper afford a means of computing energies of dissociation and bonding energies from activation energies, provided the mechanism of the reaction and something about the properties of the reactants and products is known.

Let us now consider the decomposition of the azo compounds. Azomethane,[29a] methylazoisopropane[29b] and isopropylazoisopropane[29c] are homologues that decompose unimolecularly with activation energies of 52,440 cal., 47,480 cal. and 40,900 cal., respectively. Recent investigations have shown that the most probable mechanism for these reactions involves the breaking of a C–N bond with the formation of free radicals,[30] so we assume that the reverse reaction requires no activation energy and Eqs. (6a, b) are applicable.

Although there are no data on the vibrational frequencies of the azo compounds, some estimate of the frequencies involved can be made by considering the frequencies in compounds containing equal numbers of heavy atoms. Examination of data obtained from Raman and infrared absorption spectra[31] indicates that the larger the molecule the lower the frequency of the transverse vibrations, and hence the more temperature vibration and the less zero point energy per oscillation in the molecule. Since the reaction products are smaller than the decomposing molecule, it is seen that decomposition will necessarily be accompanied by a decrease in temperature vibration (more or less counterbalanced by the increase in translational and rotational energy) and an increase in vibrational energy.

As a rough first approximation we might assume that on decomposition all the frequencies remain unchanged except four transverse vibrations, one longitudinal vibration, and one free (classical) rotation that are converted into six classical degrees of freedom, three of translation and three of rotation. For a compound with four heavy atoms these frequencies will be on the order of 600 cm^{-1} as in cyanogen (or perhaps a little lower, since there are triple bonds in cyanogen), while for eight heavy atoms they may be as low as 200 cm^{-1}. Using these figures we will have for methylazomethane at 600°K,

$$\begin{aligned} &\bar{\epsilon}_A+\bar{\epsilon}_B-\bar{\epsilon}_{AB}\sim 0.3 \text{ kg cal. per mole},\\ &\epsilon_A^\circ+\epsilon_B^\circ-\epsilon_{AB}^\circ\sim -4.3 \text{ kg cal. per mole},\\ &\epsilon_{a,\,0}=\Delta E_0\sim\epsilon_a-0.3=52.1 \text{ kg cal. per mole},\\ &\mathfrak{E}\sim\epsilon_a+4.0=56.4 \text{ kg cal. per mole}, \end{aligned} \tag{12a}$$

[25] We refer to calculations by the variation method which manipulate the electronic wave functions holding the distance between nuclei fixed.

[26] Eyring, J. Am. Chem. Soc. **54**, 3202 (1932).

[27] Eyring, Frost and Turkevich, J. Chem. Phys. **1**, 783 (1933); also see Van Vleck, ibid. **2**, 24 (1934); Mulliken, ibid. **1**, 500 (1933).

[28] Heitler and Schuchowitzki, Phys. Zeits. d. Sow. **3**, 241 (1933).

[29] Ramsperger, (a) J. Am. Chem. Soc. **49**, 912, 1495 (1927); (b) **51**, 2134 (1929); (c) **50**, 714 (1928). The energies of activation used are those calculated by Kassel, reference 3 (d).

[30] Leermakers, J. Am. Chem. Soc. **55**, 3499 (1933); F. O. Rice and Evering, ibid. **55**, 3898 (1933).

[31] Andrews, Phys. Rev. **36**, 548 (1930); Kohlrausch, *Der Smekal-Raman Effekt*, pp. 304 ff. Springer, 1931.

and for isopropylazoisopropane

$$\begin{aligned}&\bar{\epsilon}_A+\bar{\epsilon}_B-\bar{\epsilon}_{AB}\sim-1.7 \text{ kg cal. per mole},\\&\epsilon_A{}^\circ+\epsilon_B{}^\circ-\epsilon_{AB}{}^\circ\sim-1.4 \text{ kg cal. per mole},\\&\epsilon_{a,\,0}=\Delta E_0\sim\epsilon_a+1.7=42.6 \text{ kg cal. per mole},\\&\mathfrak{E}\sim\epsilon_a+3.1=44.0 \text{ kg cal. per mole}.\end{aligned}\tag{12b}$$

It is thus seen that ΔE_0 and $\mathfrak{E}$ are different for the two azo compounds, and methylazoisopropane will be intermediate. It does not seem possible that any reasonable assumption as to the frequencies could bring the values of $\mathfrak{E}$ together. If, however, there is a somewhat more profound alteration of frequencies, i.e., a general shifting to higher values, when the molecule decomposes (which is not beyond the realm of possibility) the values of ΔE_0 may be closer together, as we shall show. We still assume that the longitudinal vibrations of the hydrogens are more or less independent of the size of the molecule. As to the rest of the vibrations, we assume in the case of azomethane that we have 18 vibrations of average frequency 1000 cm^{-1} (which may be taken to include the free rotations in this case) going into twelve vibrations of average frequency 1100 cm^{-1} and six classical degrees of freedom, which gives us $\bar{\epsilon}_A+\bar{\epsilon}_B-\bar{\epsilon}_{AB}$ $\sim$1.3 kg cal. per mole at 600°K. If for isopropylazoisopropane we assume that we have 46 vibrations of average frequency 700 cm^{-1} going into 40 vibrations of average frequency 1000 cm^{-1} and 6 classical degrees of freedom we get $\bar{\epsilon}_A+\bar{\epsilon}_B$ $-\bar{\epsilon}_{AB}\sim-6.3$ kg cal. per mole. We get for methyl azomethane $\epsilon_A{}^\circ+\epsilon_B{}^\circ-\epsilon_{AB}{}^\circ\sim-6.8$ kg cal. per mole and for isopropylazoisopropane $\epsilon_A{}^\circ+\epsilon_B{}^\circ$ $-\epsilon_{AB}{}^\circ\sim11.1$ kg cal. per mole; therefore for methylazomethane

$$\begin{aligned}&\epsilon_{a,\,0}=\Delta E_0\sim\epsilon_a-1.3=51.1 \text{ kg cal. per mole}\\&\mathfrak{E}\sim\epsilon_a+5.5=57.9 \text{ kg cal. per mole}\end{aligned}\tag{13a}$$

while for isopropylazoisopropane

$$\begin{aligned}&\epsilon_{a,\,0}=\Delta E_0\sim\epsilon_a+6.3=47.2 \text{ kg cal. per mole}\\&\mathfrak{E}\sim\epsilon_a-4.8=36.1 \text{ kg cal. per mole}.\end{aligned}\tag{13b}$$

So with these assumptions we have made ΔE_0 the same for the two compounds, almost within the limits of experimental error, while the difference in the $\mathfrak{E}$ values is much increased.

We feel, however, that the assumptions made, though by no means out of the question, may be a little extreme in the direction of making the average frequencies change too much on reaction. The assumptions resulting in Eqs. (12a, b) may also be too extreme, but tending in the opposite direction. We may thus feel reasonably certain that the true values for ΔE_0 and $\mathfrak{E}$ lie between those we have obtained, provided the reaction mechanism we have taken is correct.

The matter of the reaction mechanism is one of some importance, and, unfortunately, one that cannot be definitely settled at the present time. We might, for example, have the azo compounds breaking into three pieces—a nitrogen molecule and two alkyl radicals—in one step. The reverse reaction would then be trimolecular, but in this case the method of calculation would not be substantially affected. On the other hand, we might suppose one bond to break, as we have hitherto assumed, but with å simultaneous rearrangement of some kind in the fragments.[32] Such a rearrangement might well differ as between a methyl and an isopropyl compound, and one might perhaps invoke something of this sort to explain the difference in the $\mathfrak{E}$ values we have found. And if, in addition, some of the energy of activation is thrown back into the molecule in the process of this rearrangement, and left localized at or near the place which breaks, then of course our calculations would not be justified. For then the recombining radicals would, by the principle of microscopic reversibility, also require an energy of activation and we should be barred from making any very effective calculation by the same difficulty which arose in connection with the earlier theories, namely the difficulty of calculating the fraction of molecules with a given total energy which have a certain amount of energy localized in some particular way.

Be that as it may it seems reasonable to conclude from the examples we have given that, in cases where a bond is broken and other complications do not come in, the quantum theory of Kassel is to be preferred as a first

[32] Such a rearrangement is postulated in theories of chemical binding advanced by Heitler and Schuchowitzki, reference 26.

approximation over that of Rice, and we may judge the order of magnitude of the correction (to get $\epsilon_{a,0}$ from ϵ_a) which is needed, it being much smaller than demanded by Rice's theory. Furthermore, in cases where the activation energy of the reverse reaction is small or negligible, we see how to calculate the important quantity $\mathfrak{E}$, which was not considered at all in the older theories.

Though difficulties might arise similar in nature to the possibilities discussed in the last paragraph but one, we nevertheless believe that it is very probable that considerations like those applied to the azo compounds may be used in discussing the decompositions of hydrocarbons into hydrogen and an unsaturated compound, in spite of the fact that it obviously does not involve simply the breaking of a single bond, but rather the splitting off in one step of a hydrogen molecule. In this case, of course, the reverse reaction requires an activation energy but this is probably largely the relative translational energy necessary to get the hydrogen molecule over a potential energy hill. It may also involve an excitation of the vibrational energy of the hydrogen, but if it does not involve any localization of energy in the unsaturated molecule in order for the hydrogen to unite with it, it seems very reasonable to suppose that the probability that the hydrogen will stick will be very nearly independent of the amount of energy the system may have, provided only that the relative translational energy and the vibrational energy of the hydrogen be at least equal to the minimum. Since no carbon atoms split off in this reaction, it is probable that the average vibrational frequency is in this case the same before and after the reaction, and it is very probable that $\epsilon_{a,0}$ and $\mathfrak{E}$ are both essentially equal to the value of ϵ_a at the temperature of reaction. Thus in this case, Kassel's quantum theory would be correct. The values of ϵ_a for the dehydrogenation of propane and *n*-pentane have been determined by Marek and McCluer to be 61.8 and 46.5 kg cal. per mole, respectively, which are to be compared to 73.0 for ethane. In this case while $\mathfrak{E}$ varies from one compound to another, it is seen from the heats of combustion, which are known, that ΔE_0 is constant from compound to compound.[33] Thus, though the activation energies of the forward and reverse processes in the hydrogenation of the hydrocarbons differ from one compound to another, their differences remain constant. Just why this should be the case is not at present clear.

In this connection two series of compounds studied by Coffin,[34] in which the activation energy ϵ_a seems to remain constant from compound to compound, are of interest. To explain these data, Coffin has adopted the assumption made on different grounds by Rice and Ramsperger and by Rice[35] that a molecule may be divided into reactive and nonreactive sections (the latter having little or nothing to do with the part of the molecule which actually reacts) and he has offered a new definition of activation energy as "the difference between the average energy of the reactive sections which react and the average energy of all the reactive sections." This definition necessitates such a complete separation of the sections that absolutely no exchange of energy between reactive and nonreactive sections can take place; nor can the various sections affect each other's vibration frequencies. It seems doubtful to us whether as strict a separation as this can exist, and the parts still be tied together at all. Further, in view of the considerations of this paper, it is our feeling that the data do not warrant a reformulation of the definition of activation energy, for given this new definition it would again be necessary to go through an analysis such as has been given in Part I of this paper, treating the average energies of the reactive parts instead of the whole molecules, and $\epsilon_{a,0}$ and $\mathfrak{E}$ for the series of reactions would have to be calculated before any comparisons could be made. In the cases discussed by Coffin, for example the decompositions of butylidene diacetate and ethylidene diacetate, the fact that the absolute rates are different at the same temperatures, while the activation energy is the same, indicates to him that the respective homologues have different numbers of degrees of freedom in their active parts. If this were so the average energies of the reactive parts of the homologues would be different and it is difficult to see offhand why the differences between these quantities and the average energies of the activated parts of the molecules that actually react should be the same for the homologues. For these reasons it is our opinion that the data of Coffin should be treated on the same basis as the other reactions we have discussed. There is so little basis at present for estimating the vibrational frequencies of these molecules that we have made no attempt to find $\epsilon_{a,0}$ and $\mathfrak{E}$, but we feel that ultimately this must be done to establish the validity of any interpretation of the constancy of the observed activation energy. It seems very likely, however, in these cases, in which the group of atoms added as one goes from one member of a homologous series to the next member is small compared with the whole molecule, that the values of $\epsilon_{a,0}-\epsilon_a$ and $\mathfrak{E}-\epsilon_a$ will not differ much from one member of the series to the next, so that the fact that ϵ_a remains constant is really significant. In fact, it seems more likely to be significant if we disregard Coffin's suggestion that the molecules are so completely divided into separate portions, than if we take it into consideration.

These examples of the application of the equations of Section II, will serve to illustrate what we hope may be done with much better success when more experimental data become available. As our knowledge of vibrational frequencies and specific heats of complex molecules grows,

[33] From the data of Kharasch, Bur. Standards J. Research **2**, 359 (1929), the heats of hydrogenation of both propylene and butylene can be calculated to be 32 kg cal. as compared with the 31 kg cal. experimentally determined for ethylene.

[34] Coffin, J. Chem. Phys. **2**, 48 (1934); Can. J. Research **6**, 417 (1932).

[35] (a) Rice and Ramsperger, J. Am. Chem. Soc. **50**, 619 (1928); (b) Rice, Zeits. f. physik. Chemie **B7**, 226 (1930).

the usefulness of our equations will continually increase. It is to be noted that in the derivation of Eqs. (6a) and (6b) no assumptions have been made regarding the mechanism of energy exchange within the molecule or the number of degrees of freedom involved in the reaction. It is hoped, therefore, that these equations may serve as testing blocks for theories of unimolecular reaction based upon the statistics of the dissociating molecule, and perhaps suggest new approaches to the solution of this important problem.

IV. Dependence of the Rate Constant on the Pressure

In the foregoing portions of the paper we have confined ourselves to considerations involving only the *average* energy of the reacting molecules. The theories of Rice and Ramsperger, Kassel and Rice were, however, chiefly concerned with determining the change of the rate constant with pressure, and this involves a detailed consideration of the energy distribution in those molecules which react, and the determination of the probability $b(\epsilon)$ that a molecule of given energy, ϵ (or ϵ_{AB}, but we will omit the subscript for simplicity), will react. To determine $b(\epsilon)$ it was necessary, as we have noted, to make some rather artificial assumptions; we shall now show how the considerations of this paper allow $b(\epsilon)$ to be determined if recombination of the parts in the reverse bimolecular reaction is independent of the total energy of those parts. This last condition is equivalent to the assumption that ϵ_a' is zero (but if it is necessary for the colliding particles to have a certain relative kinetic energy to get over a potential hill, and once they have this energy the probability of their recombining is independent of the excess energy, the indicated modification is readily made). With $\epsilon'_{a,\,0}$ equal to zero, if a molecule of energy ϵ decomposes (ϵ, of course, does *not* include the zero point energy) it will go over into a pair of molecules whose total energy, above their zero point energy, is $\epsilon-\epsilon_{a,\,0}$. Now we let the equilibrium fraction of all undissociated molecules with energy between ϵ and $\epsilon+d\epsilon$ (i.e., the distribution function of the molecules) be $W(\epsilon)d\epsilon$, and we let the corresponding equilibrium fraction of such pairs of the colliding dissociated molecules as have a combined energy between $\epsilon-\epsilon_{a,\,0}$ and $\epsilon-\epsilon_{a,\,0}+d\epsilon$ be $F(\epsilon-\epsilon_{a,\,0})d\epsilon$. Then by the assumptions we have made and the principle of microscopic reversibility, we must have

$$b(\epsilon)W(\epsilon)=k_1F(\epsilon-\epsilon_{a,\,0}), \tag{14}$$

where k_1 is a constant which contains a steric factor and a collision number. From this $b(\epsilon)$ may be calculated and the result may then be inserted into the general equation of Rice and Ramsperger.[36]

This differs from the result of the old theories only in the nature of the distribution function on the right. According to Kassel's classical and quantum theories $W(\epsilon-\epsilon_{a,\,0})$ would replace $F(\epsilon-\epsilon_{a,\,0})$. This is also approximately true of the classical theory of Rice and Ramsperger, while the quantum theory of Rice would demand quite a different distribution function.

There is some evidence, however, as mentioned in the last section, for the supposition that in certain cases only a limited number of degrees of freedom are directly concerned in the reaction,[35] that is only these particular degrees of freedom transmit energy freely to the bond which is to break in the reaction, and the rest of the molecule exchanges energy only slowly with this which may be called the active part of the molecule. At first sight then it might appear that the characteristics of the reaction, at reasonably high pressures (so long as only a negligible portion of the activation of the active part is due to the slow transfer of energy from the inactive part), would depend only on the properties of the active part. That this cannot be strictly true, however, is evident from the fact that the general equations of this paper contain only quantities which refer to the whole molecule. That nevertheless no contradiction can arise will appear from the following calculation.

In the case under consideration it will be seen that the quantity $b(\epsilon)W(\epsilon)d\epsilon$ will be replaced by

$$d\epsilon\int_0^{\epsilon}W^i(\epsilon-\epsilon_c)W^c(\epsilon_c)b(\epsilon_c)d\epsilon_c, \tag{15}$$

where $W^c(\epsilon_c)d\epsilon_c$ is the probability that the active part of the molecule contain an energy between ϵ_c and $\epsilon_c+d\epsilon_c$, while $W^i(\epsilon-\epsilon_c)d\epsilon$ is the probability that the inactive part of the molecule have an energy between $\epsilon-\epsilon_c$ and $\epsilon-\epsilon_c+d\epsilon$, and $b(\epsilon_c)$ is the probability that the molecule react provided the energy of the active part

[36] Reference 3a, p. 1622, Eq. (8).

is ϵ_c. (This last quantity, it will be observed, is entirely independent of the condition of the inactive part of the molecule which is of course the important characteristic of any theory which distinguishes between an active and an inactive part.) That the above expression is the one which should replace $W(\epsilon)b(\epsilon)d\epsilon$ is readily seen from the fact that $W^i(\epsilon-\epsilon_c)W^c(\epsilon_c)d\epsilon_c d\epsilon$ can be shown[37] to be the probability that the active part have energy between ϵ_c and $\epsilon_c+d\epsilon_c$ *and* the whole molecule have energy between ϵ and $\epsilon+d\epsilon$. The integral will therefore give the entire contribution to the reaction which comes from molecules whose total energy lies between ϵ and $\epsilon+d\epsilon$. The expression (15) therefore may be set equal to $k_1F(\epsilon-\epsilon_{a,0})d\epsilon$, and $b(\epsilon_c)$ may be obtained by solution of the integral equation thus set up.

Let us now compare this with what would be expected from the simplest of the older theories, namely the classical or the quantum theory of Kassel, on the assumption that in the calculation of $b(\epsilon_c)$ the inactive part is to be treated as though it were non-existent, and the calculation made on the assumption that the active part of the molecule is the whole thing. According to these theories of Kassel we should have on this basis

$$\begin{aligned} b(\epsilon_c) &= k_2W^c(\epsilon_c-\epsilon_{a,0})/W^c(\epsilon_c), && \text{if } \epsilon_c>\epsilon_{a,0} \\ &= 0, && \text{if } \epsilon_c<\epsilon_{a,0} \end{aligned} \tag{16}$$

where k_2 is a constant.

Substituting (16) into (15) we get

$$k_2d\epsilon\int_0^{\epsilon} W^c(\epsilon_c-\epsilon_{a,0})W^i(\epsilon-\epsilon_c)d\epsilon_c. \tag{17}$$

But since $W^c(\epsilon_c-\epsilon_{a,0})$ is zero for $\epsilon_c<\epsilon_{a,0}$ we have from (17), if we let $\epsilon_c=\epsilon_{a,0}+x$,

$$k_2d\epsilon\int_0^{\epsilon-\epsilon_{a,0}} W^c(x)W^i(\epsilon-x-\epsilon_{a,0})dx. \tag{18}$$

This can be seen to be equal to $k_2W(\epsilon-\epsilon_{a,0})d\epsilon$, for the integrand (if we include the factor $d\epsilon$) is equal[37] to the probability that the active part of the molecule have energy between x and $x+dx$ and the whole molecule have energy between $\epsilon-\epsilon_{a,0}$ and $\epsilon-\epsilon_{a,0}+d\epsilon$. Therefore, if the two theories were to agree, we should have

$$k_2W(\epsilon-\epsilon_{a,0})=k_1F(\epsilon-\epsilon_{a,0}). \tag{19}$$

This shows that the amount by which the results of the two theories will differ will depend only upon the difference in the energy distribution for the direct and the reverse reactions, as before, and that it is the entire energy of the molecule, not of any part, which comes into consideration, and insofar as (19) is a good approximation, (16) may also be taken as a good approximation. This conclusion has an application in forthcoming work by Rice and Sickman, for their work is based on an assumption equivalent to (16).

The above deductions are, as stated above, based on the assumption that activation and deactivation of the active part is by collision with other molecules, rather than due to the slow leakage of energy from or to the inactive part. At very low pressures, however, the latter mode of activation will be dominant, and may cause a second apparently unimolecular stage of the reaction to appear at pressures so low that the true high pressure unimolecular rate constant has already dropped off. This has been discussed by Rice[35b] and will be discussed by Rice and Sickman in more detail. What we wish to note at this place is that a very peculiar effect comes into play in this low pressure region. If two free radicals unite, the active part becomes deactivated by leakage of energy to the inactive part (from which it is eventually removed by collision). But if the energy of the two free radicals is high we may expect that enough energy will find its way back to the bond which breaks in the reaction *before* it is removed from the inactive part by collision, so that the molecule will decompose again. Such a molecule cannot truly be said to have been formed, and should not be counted when we reckon the rate of recombination. Thus the probability will depend, and depend strongly on the energy of the colliding molecules, i.e., k_1 will not be independent of ϵ, and the considerations of the preceding paragraphs will not hold. Thus we can draw no conclusion here about the temperature coefficient of the low pressure unimolecular stage.

[37] For the treatment of a similar problem see reference 3a, p. 1622.

Determination of the Speed of Flames and the Temperature Distribution in a Spherical Bomb from Time-Pressure Explosion Records[1]

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A method has been developed for determining the velocity of flame relative to the mass movement of the gases, in a closed spherical bomb from an analysis of the time-pressure record of the explosion. The speed of the flame can be evaluated at any moment during its progress from the center to the periphery of the bomb, as well as the temperature existing in the unburned phase, the temperature immediately behind the flame front, the temperature gradient from the latter point to the center of the bomb, and the pressure in the bomb at the same moment. Given a certain fraction burned of the total amount of gas, the volume occupied by the products can be determined for three conditions: (1) Before it has expanded against the rest of the unburned gas; (2) after it has expanded; and (3) when combustion is complete and it has been compressed by subsequent burning of gas nearer the periphery. Calculations of flame speeds, temperatures, etc., have been made and tabulated for explosions of mixtures of ozone and oxygen. The speed of flame increases from the center of the bomb to the wall. At the same time the pressure and temperature of the gas about to be burned increases. The temperature gradient in the gas from the center to the wall has been calculated when the combustion is complete. A complete diagrammatic description is given for one explosion. It is shown that the temperature gradient actually existing in the bomb does not affect the specific heat results obtained by the usual method of calculating the final temperature from the maximum pressure by means of the gas law. It is pointed out that the practical coincidence of the pressure curve with the zero line in the first part of the time-pressure record is not due to a time lag between passage of the spark and ignition, but to the small fraction of gas which has burned during this time.

INTRODUCTION

A METHOD of measuring the velocity of flames was successfully developed by Stevens.[4] It consists of igniting a combustible gas mixture at the center of a soap bubble and photographing the spherical flame as it expands at constant pressure. The method is simple and direct. It eliminates the serious disadvantages of flame-speed measurements in tubes, but it suffers from certain limitations. First, it cannot be used for gases that attack or are affected by a soap film. Second, the gases are necessarily always contaminated with water vapor.

On the other hand, time-pressure diagrams obtained from explosions in a closed spherical vessel can be analyzed successfully for the determination of flame speeds. The advantages of the soap-bubble method are preserved, while its disadvantages are eliminated. Experimentally, the method is both simple and applicable in general. It will be apparent from the following that a single explosion record provides a whole series of data on the explosive mixture under consideration, from which can be determined the flame speeds at different temperatures and pressures, the specific heats of the burned[5] and unburned gases[6] separately, the temperature of the unburned gases, and the distribution of temperature in the burned gases at any time during the explosion up to and including the time the flame reaches the wall.

The experimental procedure has been described in detail elsewhere.[7] Briefly, it consists of measuring the increase in pressure during the explosion of a gas mixture ignited at the center of a closed spherical bomb. The change of pressure with time was recorded on a rotating film by the movement of a light point resulting

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[4] F. W. Stevens, J. Am. Chem. Soc. **48**, 1896 (1926).

[5] Lewis and von Elbe, J. Am. Chem. Soc. **55**, 511 (1933).

[6] See following paper, p. 291.

[7] Lewis and von Elbe, J. Am. Chem. Soc. **55**, 504 (1933).

from the deflection of a specially constructed diaphragm manometer.

When a gas mixture is ignited at the center of the bomb the flame spreads spherically and concentrically toward the wall. Since the flame movement is slow compared to the velocity of sound, pressure equilibrium is considered to prevail at all times. The gases burning initially at the center of the vessel expand to a pressure, P, compressing thereby the unburned phase ahead. The work done on the unburned phase raises its temperature from its initial to some higher value. The burned phase loses an amount of thermal energy equivalent to the work done. As the flame progresses the pressure increases, further compressing the unburned phase as well as the burned phase; in consequence the temperatures of both phases are increased.

The principal object of this report is to determine the velocity of the flame relative to the moving unburned gas at any point in the enclosed sphere or, in other words, the velocity of propagation of the reaction zone into the unburned gas if the latter is considered to be at rest. This is the true speed of the flame. It is smaller than the flame velocity relative to the fixed coordinates of the bomb by an amount equal to the mass movement of the gases.

Development of the Method

The first step toward solution of the problem is to develop the relation between the amount of gas burned up to a certain time and the pressure established at that time. From this equation and the experimental time-pressure record of the explosion the amount of gas burned during any time interval can be calculated. This amount of gas will be understood to occupy an annular shell. If the time interval is the unit of time, then the thickness of this shell just before burning represents the distance the reaction zone penetrates into the unburned gas in unit time, that is, the desired flame velocity. The thickness of the shell can be calculated only when the amount of gas contained in it, the prevailing pressure, and the radius of the shell and its temperature are known. The latter is the temperature of the unburned phase.

The relation between pressure and the amount of gas burned has been developed by Mache.[8, 9] In reproducing this equation we shall employ more familiar symbols relating to mols instead of unit masses, as used by this author. Let

V = the total volume of the bomb.

v_b = the volume of the burned gas at pressure P.

v_i = the volume that the mass of gas enclosed in v_b occupied before ignition at initial pressure P_i and initial temperature T_i.

P_e = the final pressure (maximum) established when the entire contents of the vessel have reacted.

C_b and C_u = the mean molar heat capacity of the burned and unburned gases, respectively, at constant pressure between temperatures T_{bi} and T_b and T_i and T_u, respectively, where T_u is the temperature of the unburned phase and T_b is the temperature bordering directly on the burned side of the reaction zone. T_b is identical with the temperature the gases reach when allowed to burn at constant pressure at temperature T_u. Likewise T_{bi} is the temperature reached when the gases burn at constant pressure at temperature T_i.

γ_b and γ_u = the ratios of heat capacities at constant pressure and constant volume of the gases in the burned and unburned phases, respectively, for the same temperature ranges as C_b and C_u.

n_u and n_b = the number of mols per unit mass of unburned and burned gases, respectively.

In general, indices i (initial) and e (end) refer to the states before ignition and after complete combustion, while indices u (unburned) and b (burned) refer to the unburned and burned phases during the progress of the combustion from the center to the wall of the bomb.

Furthermore Mache introduces the relation

$$(n_b/n_u)C_bT_b - C_uT_u = K, \qquad (1)$$

where K is a constant. The only assumption is that mean molar heat capacities C_b and C_u are practically constant over a narrow range of temperature. For C_u the maximum range of temperature extends from T_i to the temperature of the unburned phase at its maximum compression, namely, T_{ue}. Correspondingly, the maximum range of temperature for C_b extends from T_{bi} to T_{be}, the latter of which is the temperature reached when combustion (at the end) takes place at constant pressure at temperature T_{ue}. Neither C_b nor C_u are exactly constant in

[8] L. Flamm and H. Mache. Wien. Ber. **126**, 9 (1917).

[9] H. Mache, *Die Physik der Verbrennungserscheinungen*, 1918.

this temperature span (100° to 200°), but for all practical purposes Eq. (1) appears to be fulfilled, as will be shown later.

Then if v_i/V is the fraction of the total gas burned at the time pressure P is established,

$$\frac{v_i}{V}=1-\frac{RT_i(P_e/P_i-P/P_i)}{RT_u(\gamma_b-\gamma_u)/(\gamma_u-1)+(\gamma_b-1)K}, \quad (2)$$

where R is the gas constant.

The fraction v_i/V must equal 1 when $P=P_e$ and zero when $P=P_i$. The first condition is met by Eq. (2). The second condition allows the determination of K by Eq. (2) using pressure and temperature data of an actual explosion experiment. One must demand that this value of K agree reasonably well with the value of K calculated by Eq. (1) using band spectra specific heats. Furthermore, the practical constancy of C_b and C_u must be demonstrated by the agreement in the values of K calculated by Eq. (1) for different combinations of T_b and T_u. These comparisons will be made later in the application of the method to gaseous ozone explosions.

T_u is given by the adiabatic law:

$$T_u=T_i(P/P_i)^{(\gamma u-1)/\gamma u}. \quad (3)$$

T_b is given by the thermodynamic relation:

$$T_b=(q_p/(n_b)Cp_{T_u}{}^{T_b})+T_u, \quad (4)$$

where q_p is the heat liberated per unit mass of gas at constant pressure and $Cp_{T_u}{}^{T_b}$ is the mean molar heat capacity of burned gas at constant pressure between T_u and T_b.

It may be desirable to show briefly how Eq. (2) was obtained.

Consider the mass of gas at pressure P enclosed in an elementary volume dv_u in the form of an annular shell. Before the gas is burned it is compressed by the rising pressure, according to the adiabatic law,

$$P^{1/\gamma u}dv_u=\text{constant}=P_i{}^{1/\gamma i}dv_i, \quad (2a)$$

where dv_i is the shell volume occupied by the same mass of gas before ignition occurred. It appears from Eq. (2a) that the change of state of the unburned phase is unambiguously given by the initial conditions for any pressure P. When the mass of gas in the element considered burns, it suddenly changes its volume and temperature. Its subsequent changes of state with increasing pressure in the vessel are governed by the same adiabatic compression law, namely,

$$P^{1/\gamma b}dv_b=\text{constant}. \quad (2b)$$

However, the conditions existing when this subsequent compression starts are different for the various burned shells, considering that the innermost shells, for example, burn practically at pressure P_i from an initial temperature close to T_i while the shells near the wall burn practically at pressure P_e from an initial temperature close to T_{ue}.

In order to apply the adiabatic compression law to a shell after it has burned, its temperature, T_b, immediately after burning must be known. For this purpose Mache introduces Eq. (1). Eqs. (1), (2a) and (2b) in conjunction with the condition of constancy of the total mass and volume, transform to Eq. (2) by a series of mathematical operations.

It can readily be shown that at the moment maximum pressure is established the gas is hotter in the center than it is near the wall.[10] An elementary mass of gas at the center burns by expanding at practically constant pressure P_i. It is subsequently compressed to nearly its original volume by the combustion of the rest of the gas in the vessel. The latter work of compression exceeds the former work of expansion because the compression of the elementary mass takes place at a steadily increasing pressure from P_i to P_e, while the expansion takes place at the lowest pressure P_i. An elementary mass of gas near the wall, on the other hand, is first compressed under a pressure which rises from P_i to P_e and then expands (on combustion) to approximately its original volume at the maximum pressure P_e. The latter work of expansion is obviously larger than the former work of compression. Thus the elementary mass of gas near the wall loses some of its energy while the elementary mass of gas in the center gains energy in excess of the chemical energy released within it.

The radius of any shell is calculated as follows. According to the gas law, the total number of

[10] Experimental proof of a temperature gradient was first given by Hopkinson, Proc. Roy. Soc. **A77**, 387 (1906).

mols in the bomb before ignition is given by

$$N_u = VP_i/RT_i. \tag{5}$$

The number of mols left unburned at any instant is given by $N_u(1-v_i/V)$. The volume occupied by this number of mols is $(V-v_b)$. By using the gas law once more,

$$(V-v_b)P = N_u(1-v_i/V)RT_u. \tag{6}$$

Substituting Eq. (5) and transposing,

$$\frac{v_b}{V} = 1-\frac{P_i}{P}\frac{T_u}{T_i}\left(1-\frac{v_i}{V}\right). \tag{7}$$

Since v_b is the volume of a sphere containing the expanded burned gas, its radius r_b is given by

$$\frac{r_b}{r_0} = \left[1-\frac{P_i}{P}\frac{T_u}{T_i}\left(1-\frac{v_i}{V}\right)\right]^{\frac{1}{3}}, \tag{8}$$

where r_0 is the radius of the bomb.

The flame speed is derived from these relationships as follows: From Eq. (2) find r_i, the radius of the burned phase when no expansion whatsoever occurs, that is, $r_i/r_0 = (v_i/V)^{\frac{1}{3}}$. Plot r_i against time, the latter being known from the time-pressure record. Draw three more graphs in order to correlate T_u, P, and ratio r_i/r_b, plotting these variables against r_i. From the first plot the differential quotient dr_i/dt is obtained as a function of r_i. As indicated above, dr_i/dt represents the thickness of a shell about to be traversed by the flame front in unit time under the condition that no expansion of the adjacent burned phase occurred; that is, the temperature and pressure of the shell are T_i and P_i. But by expansion the radius of the burned phase has increased from r_i to r_b, the pressure to P, and the temperature of the unburned phase to T_u. The volume of this shell of thickness, dr_i/dt before expansion of the burned phase, was

$$(dr_i/dt)4\pi(r_i)^2, \tag{9}$$

while after expansion the volume of the shell is

$$\frac{dr_i}{dt}4\pi(r_i)^2\frac{T_u}{T_i}\frac{P_i}{P}. \tag{10}$$

This volume also equals

$$4\pi r_b^2 S, \tag{11}$$

where S is the actual thickness of the shell which is just about to burn and whose combustion will be complete in unit time. S therefore represents the desired velocity of the flame:

$$S = \frac{dr_i}{dt}\left(\frac{r_i}{r_b}\right)^2\frac{T_u}{T_i}\frac{P_i}{P}. \tag{12}$$

T_u, P, and r_i/r_b are obtained from the last three plots for various values of dr_i/dt.

The velocity of the flame in any part of the vessel, the initial temperature T_u of the gas about to undergo combustion, the temperature T_b immediately behind the flame front (from Eq. (4)), and the existing pressure P are now known.

Application of the Method to Gaseous Ozone Explosions

We have applied the above system of equations to explosions of mixtures of gaseous ozone and oxygen.

Ozone decomposes according to the reaction

$$O_3\ (\text{gas}) = 1\tfrac{1}{2}O_2 + \Delta H,$$

where $\Delta H = 33{,}920$ calories at 18°C and constant pressure. If a spark is passed in gaseous ozone or a mixture of ozone and inert gas, an explosion takes place whose intensity is dependent upon the degree of dilution with inert gas. In order to obtain flame speeds of the order of 10^2 to 10^3 cm per second the gaseous ozone was diluted with pure oxygen, the ratio oxygen/ozone being varied from about 1 to 4.

Designating the ratio mols O_2/mols O_3 by m and the energy liberated at constant pressure per mol of ozone by ΔH, Eq. (4) becomes

$$T_b = (\Delta H/(1.5+m)Cp_{T_u}{}^{T_b}) + T_u \tag{4a}$$

and Eq. (1) becomes

$$[(1.5+m)/(1+m)]C_bT_b - C_uT_u = K. \tag{1a}$$

We shall now present calculations of the constant K, using, on the one hand, Eq. (1a) with band spectra heat capacities and different combinations of T_b and T_u and, on the other hand, Eq. (2) with experimental pressure and temperature data from our explosions. For all practical purposes we may identify the mean molar heat capacities C_b and C_u with the true molar heat capacities of the burned and unburned

gases at the mean temperatures between T_{bi} and T_{be} and T_i and T_{ue}, respectively. Accurate values of the true heat capacity of oxygen are known.[5] The heat capacity of ozone is known from band spectra with sufficient accuracy for this purpose. (These were kindly furnished us by Dr. L. S. Kassel.)

We shall employ the results of a typical explosion, experiment 32, series 3 (3:32).

$T_i = 302°K$, $P_e = 4814$ mm Hg,
$T_{ue} = 494°K$, $P_i = 492$ mm Hg,
$T_{bi} = 1919°K$, $m = 1.016$,
$T_{be} = 2069°K$,

$$Cu_{T_i}{}^{T_u} = \frac{m}{1+m} C(O_2)_{T_i}{}^{T_u} + \frac{1}{1+m} C(O_3)_{T_i}{}^{T_u}. \qquad (13)$$

The heat capacities are at constant pressure.

$$C_{u_{302}}^{491} = (1.016/2.016)\times 7.187 + (1/2.016)\times 10.50 = 8.83 \text{ cal./deg. mol},$$

$$C_{b_{1919}}^{2069} = 9.207 \text{ cal./deg. mol.},$$

From Eq. (1a)

$$K = (2.516/2.016)\times 9.207 \times 2{,}069 - 8.83 \times 494 = 19{,}410 \text{ calories},$$

$$K = (2.516/2.016)\times 9.207 \times 1{,}919 - 8.83 \times 302 = 19{,}370 \text{ calories}.$$

From Eq. (2),

$$1 = \frac{RT_i[(P_e/P_i)-1]}{RT_i(\gamma_b-\gamma_u)/(\gamma_u-1)+(\gamma_b-1)K} = 5266/(-33+0.275K),$$

$K = 19{,}280$ calories.

The good agreement of the K values shows that Eq. (1) is fulfilled for all combinations of T_u and T_b and that Eq. (2) meets the requirements of initial conditions. Therefore values for C_u and C_b based on our explosion data may be evaluated by a simple mathematical transformation of the above equations. This procedure provides an independent method for determining the heat capacity of ozone.[11] In all the following calculations these values of C_u and C_b are employed; all values are thus based on data obtained from the experiments under consideration.

[11] Data on the heat capacity of ozone are presented in the second paper following, p. 294.

TABLE I. *Calculation of flame speed, S, in ozone explosions from time-pressure records.*

Time, sec. $\times 10^3$	P, mm Hg	P, mm Hg	$\frac{r_i}{r_b}$	r_b cm	T_u, °K	T_b, °K	S, cm per sec.
			Experiment 3:13				
$m = 3.054$, $P_i = 624$ mm Hg, $P_e = 3572$ mm Hg, $T_i = 300.0°K$							
0	624	624	0.599	1.02	300	1239	55.0
20.70	665	630	.601	2.99	301	1240	60.7
27.63	712	650	.603	4.96	303	1241	61.5
34.52	795	700	.615	7.04	309	1247	63.6
37.98	862	785	.637	8.86	317	1253	65.5
41.42	991	885	.666	10.15	327	1259	74.3
44.88	1141	1070	.702	11.33	343	1274	86.1
48.35	1353	1324	.745	12.41	361	1289	100.0
51.79	1661	1622	.791	13.20	380	1304	114.0
55.25	2155	2024	.845	13.83	401	1322	134.2
56.97	2499	2560	.907	14.38	427	1343	158.0
58.72	2948	3220	.970	14.80	451	1362	178.0
59.41	3192						
59.75	3324						
60.44	3572						
$\gamma_u = 1.328$, $Cp_{T_{ue}}{}^{T_{be}} = 8.18$, $Cp_{T_i}{}^{T_{bi}} = 7.935$, $T_{be} = 1373$, $T_{bi} = 1239$, $T_{ue} = 462$, r_i/r_b(for $P = P_i$) $= 0.599$.							
			Experiment 2:09				
$m = 1.497$, $P_i = 367$ mm Hg, $P_e = 3029$ mm Hg, $T_i = 301.1°K$							
0	367	370	0.535	1.83	301	1680	141
8.66	445	389	.546	4.96	305	1684	165
9.70	507	400	.555	6.54	307	1685	187
10.38	564	445	.568	8.20	314	1689	203
11.08	626	575	.610	10.54	333	1704	224
11.77	698	690	.638	11.48	347	1714	237
12.98	910	820	.672	12.25	361	1726	257
13.57	1045	980	.708	12.90	376	1738	282
14.34	1313	1185	.750	13.46	392	1750	314
14.89	1582	1420	.791	13.87	408	1763	352
15.31	1845	1695	.833	14.22	425	1777	395
15.62	2110	2000	.878	14.48	441	1790	435
16.17	2627	2825	.978	14.92	477	1818	563
16.30	2812						
16.52	3029						
$\gamma_u = 1.291$, $Cp_{T_{ue}}{}^{T_{be}} = 8.445$, $Cp_{T_i}{}^{T_{bi}} = 8.21$, $T_{be} = 1825$, $T_{bi} = 1680$, $T_{ue} = 484$, r_i/r_b(for $P = P_i$) $= 0.531$.							
			Experiment 3:32				
$m = 1.016$, $P_i = 492$ mm Hg, $P_e = 4814$ mm Hg, $T_i = 301.5°K$							
0	492	495	0.502	0.92	302	1922	160
5.61	663	510	.508	4.11	304	1923	219
6.30	777	575	.526	7.28	312	1928	287
7.00	958	730	.560	10.05	317	1930	309
7.52	1164	970	.607	11.76	350	1958	379
7.79	1314	1355	.675	12.95	376	1976	495
7.97	1469	2042	.765	13.92	411	2003	615
8.28	1692	2735	.840	14.32	438	2021	693
8.66	2199	3200	.880	14.55	453	2035	733
8.94	2700	3760	.925	14.76	468	2044	747
9.11	3134	4440	.975	14.92	486	2063	780
9.32	3702						
9.49	4252						
9.59	4542						
9.67	4814						
$\gamma_u = 1.276$, $Cp_{T_{ue}}{}^{T_{be}} = 8.565$, $Cp_{T_i}{}^{T_{bi}} = 8.34$, $T_{be} = 2069$, $T_{bi} = 1919$, $T_{ue} = 494$, r_i/r_b(for $P = P_i$) $= 0.500$.							

The flame speeds for a considerable number of explosions were calculated, but only the results of three representative ones will be presented, namely, a moderately slow, a medium, and a moderately fast explosion. The results are tabulated in Table I. The radius of the bomb is 150 mm.

The first column for each experiment gives the time in milliseconds at which the absolute pressure in the second column was reached. These values were obtained from the experimental time-pressure record of the explosion. The next six columns show the results calculated from the first two columns by the method given above. The sixth column of the group contains S, the flame speed relative to the moving gases at various radii, r_b, given in column 3 of this group. In column 5 of this group the corresponding T_b, calculated from Eq. (4a), is given for convenience. The $Cp_{T_u}{}^{T_b}$ in this equation may be found readily by interpolating between the two limits given for $Cp_{T_{ue}}{}^{T_{be}}$ and $Cp_{T_i}{}^{T_{bi}}$, which are indicated under each experiment in Table I and which were obtained from earlier work.[5]

r_i/r_b at the beginning cannot be determined easily from the above equations because both values approach zero. It is evaluated in the following way. Assume that a very small number of mols, dn, burns at the beginning. The volume it occupies, if no expansion occurs, equals

$$v_i = dn(RT_{\bar{e}}/P_e), \tag{14}$$

where $T_{\bar{e}}$ is the temperature calculated from the gas law and the maximum pressure P_e (see below). After expansion the temperature decreases to T_{bi} and the pressure to P_i. Then the new volume equals

$$v_b = dn(RT_{bi}/P_i). \tag{15}$$

Combining,

$$v_i/v_b = (P_i/P_e)(T_{\bar{e}}/T_b) \tag{16}$$

and

$$r_i/r_b = [(P_i/P_e)(T_{\bar{e}}/T_b)]^{\frac{1}{3}}. \tag{17}$$

Temperature Gradient in the Bomb and Its Effect on the Determination of Specific Heats by the Explosion Method

Before developing the above treatment we attempted to devise a simplified method for determining flame speeds by assuming that the temperature is equalized throughout the burned phase at any time. However, the values of T_b calculated and the values of T_b found from Eq. (4a) varied widely, indicating a rather steep temperature gradient from the center of the bomb to the wall which could not be neglected.

Mache[9] developed a formula for the temperature gradient in a spherical bomb at the instant combustion is complete. If $Te_{(vi/V)}$ is the temperature at the surface of the sphere which encloses a fraction, v_i/V, of the total gas burned, then

$$Te_{(vi/V)} = \frac{\gamma_b - 1}{\gamma_b}\,\frac{1+m}{1.5+m}\,T_i\left(\frac{P_e}{P}\right)^{(\gamma_b-1)/\gamma_b}\left[\frac{K}{RT_i} + \frac{\gamma_u}{\gamma_u - 1}\left(\frac{P}{P_i}\right)^{(\gamma_u-1)/\gamma_u}\right], \tag{18}$$

in which all the symbols are known.

In the explosion method for determining the heat capacities of gases the maximum pressure developed is used to calculate the temperature of the gases, $T_{\bar{e}}$, from the gas law under the assumption that the temperature is equalized throughout the bomb. As already pointed out by Hopkinson[10] this procedure would be strictly justified if the heat capacity of the gases did not vary with temperature. In the normal case, however, where one deals with polyatomic molecules and their dissociations the maximum pressure recorded is a little less than the maximum pressure which would have been recorded had the temperature throughout the bomb been equalized without heat loss. We have made extended calculations of this effect for the present type of explosion including the effect of dissociation and find that the difference between these pressures is from less than 0.1 percent to less than 0.3 percent in the extreme case of the highest temperature explosions. This work will be published soon.

For other types of explosive mixtures one may

estimate the effect to be very small except in explosions where large dissociation occurs. But even in such cases the pressure difference can be calculated and therefore this effect does not constitute an objection to the explosion method.

Fig. 1 shows graphically the conditions in the bomb while combustion is in progress and before and after combustion for explosion 2:09. The hemisphere represents one-half of the bomb. The abscissa is the radius of the bomb, 15.00 cm. The upper quadrant shows the positions reached by the flame front after equal time intervals. The time interval in this instance is 1.65×10^{-3} sec., which is exactly 1/10 of the total explosion time. The pressure existing in the bomb for these positions of the flame front are indicated on the left. Temperatures T_u and T_b in front of and behind the flame front, respectively, are given to the right of these. Thus the upper quadrant provides a complete picture of conditions during the progress of the flame. It should be emphasized that temperature T_u in front of the flame is equalized throughout the entire unburned phase, whereas temperature T_b behind the flame is localized in the immediate vicinity of the flame front. From the rear of each flame-front position the temperature rises toward the center of the bomb. The arrows represent flame speeds S relative to the moving gas when the flame reaches the positions indicated.

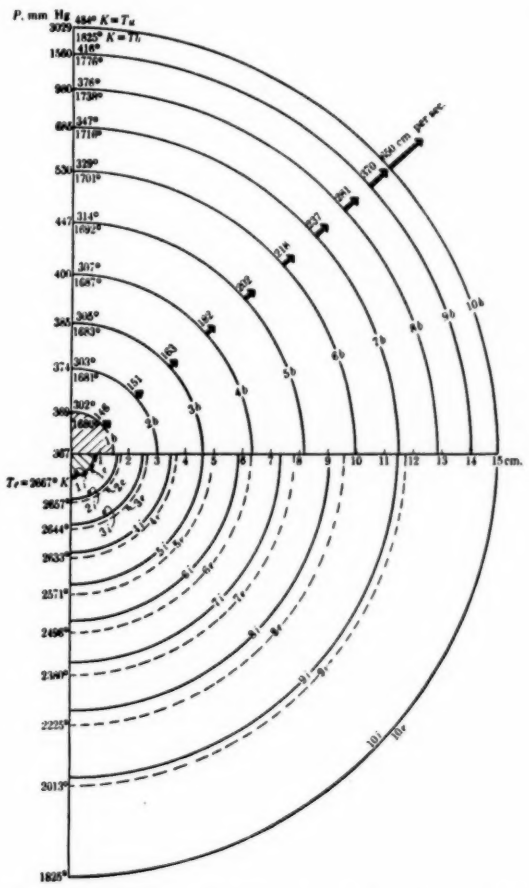

FIG. 1. Experiment 2:09. Showing the hemisphere of the bomb. Abscissa = radius of bomb in cm. Total explosion time 16.5×10^{-3} sec. Upper quadrant: Contains speed of flame in various parts of bomb. Curves marked 1*b*, 2*b*, etc., are volumes occupied by gas burned in equal time intervals, in this case 1/10 of total explosion time. Pressure in bomb, temperature T_u in unburned phase and temperature T_b immediately behind flame front when flame reaches points indicated after successive tenths of total explosion time, are given to the left. Lower quadrant: Solid curves, 1*i*, etc., are volumes occupied by same mass of gas enclosed in 1*b*, etc., for condition that no expansion of the gases occurred. Dotted curves 1*e*, etc., are final volumes occupied by same mass of gas in 1*i*, etc., or 1*b*, etc., after 1*b*, etc., has been compressed due to subsequent burning of the outer shells. Temperature gradient existing in bomb when combustion is complete, is given to the left.

The solid curves in the lower quadrant designated by numerals with the subscript i, which denotes pre-ignition conditions, mark the boundaries of the spheres occupied by the same mass of gas contained in the corresponding spheres in the upper quadrant whose boundaries are marked by numerals with the subscript b. The difference between the corresponding i and b spheres results from the expansion which occurs on combustion. The two-shaded portions represent this for the mass of gas burned during the first 1/10 of the total explosion time.

The dotted curves designated by numerals with the subscript e mark the boundaries of the spheres occupied by the same masses of gases corresponding to the i and b states after the explosion is complete or when the maximum pressure is reached. They show the extent to which the b spheres have been compressed by the subsequent combustion. The radii in centimeters of the dotted spheres were calculated from the formula given by Mache, which by a simple transformation may conveniently be written

$$r_e = r_b[(P/P_e)^{1/\gamma_b}]^{\frac{1}{3}}. \qquad (19)$$

The temperatures existing at the boundaries of these spheres after combustion is complete may be calculated from Eq. (18) for the same values

of P used in Eq. (19). These temperatures, given to the left of the lower quadrant, may be compared with temperature $T_{\bar{e}}=2072°K$, which would exist if the temperature were equalized.

The temperatures of the inner portions of gas are somewhat too high because dissociation of oxygen has been neglected in these calculations, and therefore the value of C_b used is somewhat too small. Radii r_e, however, would be affected only slightly. We believe the picture, as presented, is nevertheless substantially correct.

Table II contains the numerical data shown in Fig. 1.

Fig. 2 is a photograph of the time-pressure record of explosion 2:09 from which Fig. 1 was derived.

TABLE II. *Numerical data for experiment 2:09 used in Fig. 1.*

Time, sec. $\times 10^3$	r_i, cm	$\frac{r_i}{r_b}$	r_b, cm	T_u, °K	T_b, °K	P, mm Hg	S, cm per sec.	T_e, °K	r_e, cm
0	0	0.531	0	301	1680	367	(140)	2670	0
1.65	.79	.534	1.48	302	1680	369	146	2667	.86
3.30	1.62	.538	3.01	303	1681	374	151	2657	1.75
4.95	2.52	.544	4.63	305	1683	385	163	2644	2.71
6.60	3.52	.554	6.36	307	1687	400	182	2633	3.76
8.25	4.65	.569	8.17	314	1692	447	202	2571	4.97
9.90	5.91	.595	9.94	329	1701	530	218	2496	6.32
11.55	7.36	.640	11.50	347	1716	685	237	2380	7.81
13.20	9.10	.708	12.85	376	1738	980	281	2225	9.58
14.85	11.45	.815	14.05	416	1776	1560	370	2013	11.76
16.50	15.00	1.000	15.00	484	1825	3029	(650)	1825	15.00

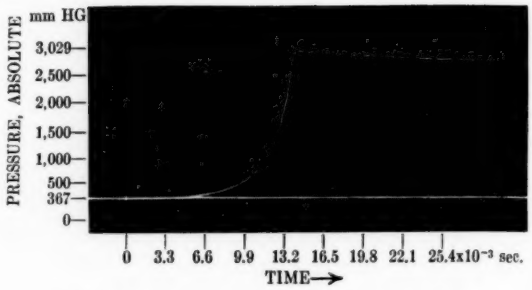

FIG. 2. Time-pressure record, explosion 2:09.

It is of interest that in the first part of the record the curve practically coincides with the zero line. It has been stated in the literature that this circumstance is due to the existence of a time lag between the passage of the spark and ignition. However, this conclusion is not admissible.[12] In the present case, for example, reference to Figs. 1 and 2 shows that when 1/5 of the total explosion time has elapsed the pressure rise becomes just readable at 7 mm Hg. In this same time the flame front has progressed 3 centimeters or 1/5 of the radius of the bomb.

[12] Payman (Fuel **1**, 36 (1922)) also realized this.

The Experimental Determination of the Heat Capacity of Explosive Gases by a New Method[1]

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(Received January 22, 1934)

A method is described for determining the heat capacity of explosive gases at temperatures up to several hundred degrees above room temperature, by exploding the gas whose heat capacity is to be determined in a spherical bomb. The same data are required as are needed to determine the heat capacity of the burned gas by the explosion method, namely, the maximum pressure developed in the explosion, the initial temperature and initial pressure, the composition of the gas mixture, and the heat of reaction. Equations have been developed, and the method is described in detail. The method is particularly useful for the determination of heat capacities of easily decomposed gases, such as O_3 and Cl_2O, for which the flow method is unsuitable. An interesting consequence of the method is that it permits simultaneous determination of the heat capacity of carbon dioxide at high and low temperatures by exploding mixtures of gaseous ozone and carbon dioxide.

HITHERTO, experiments on explosions of gases at constant volume in a spherical bomb have been utilized to determine the mean heat capacity of the *products* of the explosion between the initial temperature of the gases and the final mean temperature calculated from the maximum pressure by means of the gas law. The present paper deals with a method for employing the same explosion experiments to determine the mean heat capacity of the *reactants* between the initial temperature and the highest temperature reached by the unburned gases due to their adiabatic compression by the expanding burned gases during the explosion process.

The heat capacities of gases between room temperature and several hundred degrees above usually are determined by the flow method; however, there are gases, such as O_3 and Cl_2O, for which this method is not suitable due to the ease with which they decompose. Therefore, the method we shall describe is especially useful in such cases. One particularly interesting consequence of the method is that explosions of mixtures of ozone and carbon dioxide allow simultaneous determination of the heat capacity of carbon dioxide at high and at low temperatures.

The method is based on the principle that the work of compression done on the unburned phase and its temperature rise due to compression may be determined independently, yielding directly the heat capacity of this phase. If the original gas is composed of a single component, the heat capacity so obtained is that of this gas. If it is composed of a mixture of two gases the heat capacity of one should be known to determine the heat capacity of the other. In practice it is usually necessary to dilute the explosive mixture.

All equations needed are contained in the preceding paper.[4] The equation relating the fraction of the total gas burned with the pressure, P, in the bomb, is:

$$1-\frac{v_i}{V}=\frac{RT_i(P_e/P_i-P/P_i)}{RT_u(\gamma_b-\gamma_u)/(\gamma_u-1)+(\gamma_b-1)K}, \quad (1)$$

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[4] See preceding paper, p. 283.

where v_i is the volume of the initial gas mixture burned and V the total volume of the bomb.

v_i/V is the fraction of the total gas which has burned when the pressure, P, is established.

P_e is the maximum pressure developed in the explosion.

P_i and T_i are the initial pressure and temperature of the gas mixture.

T_u is the temperature in the unburned phase when the fraction v_i/V has burned. Thus $T_u > T_i$.

γ_u is the ratio of mean heat capacities of the unburned phase at constant pressure and constant volume between the temperatures T_i and T_{ue}, where T_{ue} is the highest temperature reached by the unburned phase just prior to complete combustion or near the wall of the bomb.

γ_b is the same ratio for the burned phase between the temperatures T_{bi} and T_{be}, where T_{bi} is the temperature reached when the gas burns at constant pressure from the initial temperature T_i, and T_{be} is the temperature reached when the gas burns at constant pressure from the initial temperature T_{ue}.

It may be remembered from the previous paper that the temperature T_{bi} or T_{be} is reached when the first or last infinitesimally small amount of gas is burned. Since the combustion of this amount of gas increases the total pressure only infinitesimally, the process takes place at constant pressure.

K is defined by Eq. (2) and is a constant.

$$K=(n_b/n_u)C_bT_b-C_uT_u, \tag{2}$$

where n_b and n_u are the number of mols per unit mass of burned and unburned gases, respectively.

C_b and C_u are the mean molar heat capacities per mol at constant pressure of the burned and unburned gases between T_{bi} and T_{be}, and T_i and T_{ue}, respectively.

Since the energy $C_u(T_{ue}-T_i)$ must equal the energy $(n_b/n_u)C_b(T_{be}-T_{bi})$, it follows that,

$$K=(n_b/n_u)C_bT_{be}-C_uT_{ue}$$
$$=(n_b/n_u)C_bT_{bi}-C_uT_i. \tag{2a}$$

The temperature T_{bi} is given by the thermodynamic relation:

$$T_{bi}=q_p/n_bCp_{T_i}{}^{T_{bi}}+T_i, \tag{3}$$

where q_p is the chemical energy liberated at constant pressure per unit mass of gas, and $Cp_{T_i}{}^{T_{bi}}$ is the mean molar heat capacity of burned gas at constant pressure between T_i and T_{bi}.

Likewise, the temperature T_{be} is given by

$$T_{be}=q_p/n_bCp_{T_{ue}}{}^{T_{be}}+T_{ue}. \tag{4}$$

The temperature T_{ue} is given by the adiabatic law,

$$T_{ue}=T_i(P_e/P_i)^{\gamma_u-1/\gamma_u}. \tag{5}$$

On imposing the condition $P=P_i$ and therefore $v_i/V=0$ in Eq. (1), dividing by RT_i, and substituting the right side of Eq. (2a) for K, one obtains,

$$1=\left(\frac{P_e}{P_i}-1\right)\Big/\left[\frac{\gamma_b-\gamma_u}{\gamma_u-1}-(\gamma_b-1)\frac{C_u}{R}+(\gamma_b-1)\frac{C_b}{R}\frac{n_b}{n_u}\frac{T_{bi}}{T_i}\right]. \tag{6}$$

Since

$$\frac{\gamma_b}{\gamma_b-1}=\frac{C_b}{R} \quad \text{and} \quad \frac{\gamma_u}{\gamma_u-1}=\frac{C_u}{R}, \tag{7}$$

then

$$\frac{\gamma_b-\gamma_u}{\gamma_u-1}-(\gamma_b-1)\frac{C_u}{R}=-\gamma_b, \tag{7a}$$

and

$$(\gamma_b-1)C_b/R=\gamma_b. \tag{7b}$$

Eq. (6) then becomes

$$\gamma_b=\frac{P_e/P_i-1}{(n_b/n_u)(T_{bi}/T_i)-1}. \tag{8}$$

Eq. (8) provides a method for determining the mean heat capacity of the burned gases between T_{bi} and T_{be} which, over this narrow range of temperature, is practically identical with the true specific heat at the mean between these temperatures.

Now repeat the operations performed in obtaining Eq. (6) but substitute for K the left side of Eq. (2a), transpose, and divide by γ_b-1. Then

$$\frac{\gamma_u-\gamma_b}{(\gamma_u-1)(\gamma_b-1)}RT_i+C_uT_{ue} = \frac{n_b}{n_u}C_bT_{be}-RT_i\left(\frac{P_e}{P_i}-1\right)\frac{1}{\gamma_b-1}. \quad (9)$$

With the relations (7),

$$(\gamma_u-\gamma_b)/(\gamma_u-1)(\gamma_b-1)=(C_u-C_b)/R, \quad (10)$$

so that Eq. (9) becomes,

$$C_u(T_{ue}-T_i)+C_bT_i = (n_b/n_u)C_bT_{be}-RT_i(P_e/P_i-1)/(\gamma_b-1). \quad (11)$$

Eq. (8) may be written

$$\frac{\gamma_b}{\gamma_b-1}=\frac{C_b}{R}=\left(\frac{P_e}{P_i}-1\right)\Big/\left(\frac{P_e}{P_i}-\frac{n_b}{n_u}\frac{T_{bi}}{T_i}\right), \quad (12)$$

and also

$$\frac{1}{\gamma_b-1}=\left(\frac{n_b}{n_u}\frac{T_{bi}}{T_i}-1\right)\Big/\left(\frac{P_e}{P_i}-\frac{n_b}{n_u}\frac{T_{bi}}{T_i}\right). \quad (13)$$

Substituting (12) and (13) in (11) and transposing,

$$C_u=\frac{R(P_e-P_i)}{(n_u/n_b)P_e-(T_{bi}/T_i)P_i}\cdot\frac{T_{be}-T_{bi}}{T_{ue}-T_i}. \quad (14)$$

C_u is the mean molar heat capacity of the unburned gas at constant pressure between T_i and T_{ue}.

If, for example, the original explosive mixture is composed of two components, l and m, having mol fractions x and $1-x$, respectively,

$$C_u=xC_l+(1-x)C_m, \quad (15)$$

where C_l and C_m are the mean molar heat capacities at constant pressure between T_i and T_{ue} of the components l and m, respectively. Practically, over this narrow range of temperature, these mean heat capacities are very nearly the true heat capacities at the mean temperature $(T_i+T_{ue})/2$.

The temperatures T_{bi}, T_{be}, and T_{ue} are determined from Eqs. (3), (4) and (5) in combination with Eq. (14) by the method of trial and error. It is necessary to know, therefore, the temperature dependency of the heat capacity of the burned gas, which is obtained by the explosion method in the usual way and for which the same experiments may be utilized. In practice, therefore, this information is available. In working out specific examples it will be found convenient to employ a plot of the mean heat capacity of the burned gas between some low standard temperature such as absolute zero, and T_b. $Cp_{T_{ue}}{}^{T_{be}}$, for example, may be found from the plot by employing the relation

$$Cp_{T_{ue}}{}^{T_{be}} = (T_{be}Cp_{T_o}{}^{T_{be}}-T_{ue}Cp_{T_o}{}^{T_{ue}})/(T_{be}-T_{ue}). \quad (16)$$

The Experimental Determination of the Heat Capacity of Gaseous Ozone[1]

BERNARD LEWIS[2] AND GUENTHER VON ELBE,[3] *U. S. Bureau of Mines*

(Received January 22, 1934)

The mean heat capacity of ozone between 300 and 476°K has been determined from explosions of mixtures of ozone and oxygen in a spherical bomb by the method the authors described in a previous paper. The value obtained is 10.94 calories per mol of ozone. The value obtained from band spectra is 10.39 calories per mol. The difference cannot be accounted for by incorrect assignment of the optical frequencies of ozone, and it is larger than the probable experimental error. It is proposed that the difference may be due to a contribution to the heat capacity of an electronic level lying close to the ground state of the ozone molecule. It is estimated that this supposed level has an energy of 0.1 to 0.2 volt. The existence of low-energy electronic levels probably implies an isosceles triangle structure and paramagnetic properties of the ozone molecule in the normal and the low excited states.

IN the preceding communication[4] a new general method for determining the heat capacity of explosive gases was described. The present paper will discuss application of the method to the determination of the heat capacity of gaseous ozone.

Mixtures of gaseous ozone and oxygen in varying proportions were ignited at the center of a spherical bomb and the maximum pressures P_e, developed were accurately measured on the time-pressure records of the explosions, as described previously.[5] Additional data needed are initial pressure P_i, initial temperature T_i, the composition of the original mixture m, which is the ratio of the concentrations of oxygen and ozone, the heat of decomposition of 1 mol of ozone at constant pressure and room temperature equal to +33,920 calories, and the mean heat capacity of oxygen at constant pressure from some convenient reference temperature (say 0°K) to the temperatures of the explosions. Other symbols used are:

T_{ue} = the temperature of the adiabatically compressed unburned gas just prior to complete combustion or near the wall of the bomb;

T_{bi} and T_{be} = the temperatures established by burning a mass of gas at constant pressure from initial temperatures T_i and T_{ue}, respectively;

C_u = mean molar heat capacity of unburned gas at constant pressure between the temperatures T_i and T_{ue};

$Cp_{T_{ue}}^{T_{be}}$ and $Cp_{T_i}^{T_{bi}}$ = the mean molar heat capacities of oxygen at constant pressure between the temperatures indicated.

The reaction which takes place is:

$$O_3\ (\text{gas}) = 1.5O_2 + 33{,}920 \text{ calories}.$$

All the equations of the preceding paper remain the same, except for modifications indicated in Eqs. (1), (2) and (3) below.

$$n_b/n_u = (1.5+m)/(1+m), \tag{1}$$

$$T_{bi} = (33{,}920/(1.5+m)Cp_{T_i}^{T_{bi}}) + T_i, \tag{2}$$

$$T_{be} = (33{,}920/(1.5+m)Cp_{T_{ue}}^{T_{be}}) + T_{ue}. \tag{3}$$

Table I summarizes the data of a group of experiments and the results of the calculations.

The last column shows the calculated mean molar heat capacity of ozone. The average of the results between 300 and 476°K is 10.94 calories per mol. The average deviation from the mean is 0.30 calorie per mol, with the value given as the most probable value.

The above result may be compared with the heat capacity of ozone calculated from existing optical data. Kassel[6] has calculated the free energy of ozone, based on Gerhard's[7] frequency

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

[3] Member of staff, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

[4] See preceding paper, p. 291.

[5] Lewis and von Elbe, J. A. C. S. **55**, 504, 511 (1933).

[6] L. S. Kassel, J. Chem. Phys. **1**, 414 (1933).

[7] Gerhard, Phys. Rev. **42**, 622 (1932).

TABLE I. *Determination of heat capacity of gaseous ozone, $Cp(O_3)$.*

Experiment No.	P_e	P_i	T_i	m	T_{bi}	T_{be}	T_{ue}	$Cp_{T_{ue}}{}^{T_{be}}$	$Cp_{T_i}{}^{T_{bi}}$	C_u	$Cp(O_2)_{T_i}{}^{T_{ue}}$	$Cp(O_3)_{T_i}{}^{T_{ue}}$
2.09	3029	367	301	1.497	1680	1825	484	8.45	8.21	8.81	7.18	11.2
2.11	2984	414	301	1.990	1500	1646.5	481.5	8.34	8.09	8.35	7.17	10.7
3.01	2295	436	302	3.471	1168	1294	464	8.14	7.88	8.11	7.17	11.3
3.12	3352	474	300	2.083	1472	1618	483	8.34	8.08	8.16	7.17	10.2
3.13	3572	624	300	3.054	1239	1373	462	8.18	7.94	8.03	7.16	10.7
3.14	3251	513	301	2.541	1350	1490.5	473.5	8.25	8.00	8.07	7.17	10.4
3.15	3296	561	300	2.890	1271	1402	460	8.20	7.96	8.18	7.15	11.1
3.16	3996	639	300	2.600	1335	1472.5	467.5	8.23	7.99	8.19	7.16	10.9
3.22	2884	368	301	1.663	1613	1756	481	8.41	8.17	8.70	7.18	11.2
3.23	2851	366	302	1.675	1610	1752.5	479.5	8.39	8.17	8.80	7.18	11.5
3.32	4814	492	302	1.016	1918	2069	494	8.57	8.34	9.18	7.19	11.2

assignment 528, 1033 and 1355 cm^{-1}, and has kindly furnished us with values of the heat capacity of ozone determined from them. Between 300 and 476°K the mean heat capacity is 10.39 calories per mol. Any reasonable change in these frequencies would hardly affect the heat capacity determined from band spectra by more than 0.05 calorie. The difference between the experimental and optical values is too great to be accounted for by experimental error. We suggest that this is due to the contribution of an electronic level lying close to the ground state of the ozone molecule.

If a reasonable assumption is made regarding the statistical weight of this level with respect to the ground level, its energy can be estimated[8] to be 0.1 to 0.2 volt.

The existence of one or more low energy electronic levels probably would imply that the ozone molecule has an isosceles triangle structure in both the normal and the low excited states and that the ozone molecule may be paramagnetic.[9] There are no measurements of the latter, but it seems to be entirely feasible to determine the magnetic susceptibility of gaseous ozone. Concerning the structure of the molecule, the most recent spectroscopic investigations[7] indicate that it is isosceles in form.

[8] Lewis and von Elbe, Phys. Rev. **41**, 678 (1932).

[9] Private correspondence with Professor R. S. Mulliken.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Zero-Point Energy of Molecular Crystals

Sufficient data are available to calculate the zero-point energy of some simple molecular crystals. These values may be compared with the corresponding heats of sublimation calculated to 0°K. The zero-point energy may be calculated from the relation:

$$E(0°K) = \int_0^{\nu\,(\max)} F\nu^3 (h\nu/2) d\nu = 2.25\theta_{(\max)} \text{ calories.}$$

The heats of sublimation were calculated to 0°K from the best recent available data. The results are given in Table I.

TABLE I.

	M.W.	$\theta_{(\max)}$	E(0°K)	ΔH(0°K)	M.P.	E(0°K)/ΔH(0°K)
He [2]	4.	9	20	24(4°K)	0.9	84%
Ne [1]	20.2	63	142	425	24.4	33.
A [1]	39.9	85	191	1830	83.9	10.
H_2 [3]	2.	91	205	216(20°K)	14.	95.
N_2 [4]	28.	68	153	1636	63.3	9.
CO [5]	28.	80	179	1845	68.1	10.
NO [6]	30.	119	268	3680	109.5	7.
O_2 [7]	32.	91	204	2083	54.7	10.
HCl [8]	36.46	128	290	4845	161.	6.
HBr [9]	80.92	92	207	5428	184.6	4.
HI [10]	127.9	73	164	6250	222.3	3.

[1] *Landolt-Bornstein Physical Tables.*
[2] Keesom and Keesom, Proc. Acad. Sci. Amst. **35**, 736 (1932).
[3] Fowler and Stern, Rev. Mod. Phys. **4**, 697 (1932).
[4] Giauque and Clayton, J.A.C.S. **55**, 4882 (1933).
[5] Giauque and Clayton, J.A.C.S. **54**, 2619 (1932).
[6] Giauque and Johnston, J.A.C.S. **51**, 3208 (1929).
[7] Giauque and Johnston, J.A.C.S. **51**, 2300 (1929).
[8] Giauque and Wiebe, J.A.C.S. **50**, 116 (1928).
[9] Giauque and Wiebe, J.A.C.S. **50**, 2200 (1928).
[10] Giauque and Wiebe, J.A.C.S. **51**, 1447 (1929).

In order for the crystal state to exist the sum of the zero-point energy, the attraction potential and the repulsion potential must be negative. From the table it is seen that the ratio of the zero-point energy to the heat of sublimation is greater for the crystal of lighter mass particles. Hence a crystal of the lighter mass particles is the less stable one, in virtue of its high zero-point energy. Further it is reasonable to say that the more negative the above-mentioned sum, the more stable is the lattice to a change of state. As evidence for this the melting points of the monatomic solids in the table increase with the heat of sublimation. Likewise do the melting points of the diatomic solids. Of the latter the value for nitric oxide suggests the existence of (N_2O_4) units. The hydrogen halide crystals have an additional factor entering into the attraction potential, namely the electrostatic potential between the permanent dipoles.

V. DEITZ*

University of Illinois,
Urbana, Illinois,
March 10, 1934.

* National Research Fellow 1933–34.

A Reaction Produced by Light of Very Short Wave-Length

When light from a capillary discharge tube filled with hydrogen at a pressure of 1–2 mm of Hg passes for some time through a fluorite window into air at atmospheric pressure there is formed on the *outside* of the window a light film showing metallic luster. The film can be removed by swabbing the window with absorbent cotton moistened with alcohol.

A more prolonged use of the tube gives rise to a deposit of white powder on top of the film which can easily be brushed off with dry cotton. Both deposits tend to prevent the passage of wave-lengths 1250–1500 Angstroms through the window. An imperfection in the fluorite casts a shadow in such a manner that no deposit is formed at a point where a straight line from the end of the capillary through

the imperfection cuts the surface of the fluorite.

The powder has been found to be insoluble in distilled water but soluble in dilute hydrochloric acid. It forms after a shorter period of time if the air is moist than if it has been carefully dried. It is possible that light of extremely short wave-length activates the oxygen of the air so that either (1) calcium oxy-fluoride (perhaps) is formed directly, or (2) hydrogen peroxide is produced first and then reacts with CaF_2 to form the deposit. In the latter case it might be expected that a very strong solution of H_2O_2 applied to the window would produce some effect upon it, but upon making this test not the slightest effect could be detected. As yet nothing further is known about the nature of the deposit or of the reaction which causes it.

FREDERIC PALMER, JR.

Haverford College,
Haverford, Pennsylvania,
March 20, 1934.

Note on the sp^3 Configuration of Carbon, and Correction to Part III on CH_4

In part III[1,2] of my recent series on CH_4, I overlooked Edlén's[3] new measurements and classifications for the spectra of C I, N II and O III, which appeared just as my article was being completed. The previously unknown $sp^3\,{}^5S$ state has been found by Edlén in N II and O III, and may now be located in carbon I at approximately 4.1 volts above the ground state $s^2p^2\,{}^3P$ by extrapolation from N II and O III with the aid of the irregular doublet law. A more accurate, in fact quite remarkable, method of extrapolation based on theoretical considerations has subsequently been developed by Bacher and Goudsmit.[4] It places ${}^5S$ at 4.3 volts in carbon. Thus ${}^5S$ is not quite as high above the ground state as my previous estimate 5–8 volts based on the Slater-Condon-Johnson *F-G* relations, but is much closer to this estimate than to the value 1.6 volts so often quoted in the literature. It is somewhat accidental that my estimate was as close as it is, for in applying these relations, I used the experimental values of the $sp^3\,{}^1D$ and $sp^3\,{}^1P$ terms, *viz.*, 9.65 and 9.66 volts, usually listed in spectroscopic tables, such as for example Bacher and Goudsmit's book.

Edlén finds that the terms at these positions are certainly due to some other configuration, probably s^2pd. The true $sp^3\,{}^1D$ and $sp^3\,{}^1P$ levels have not yet been detected spectroscopically, but may be located by Bacher and Goudsmit's new method at 12.9 and 14 volts, respectively. (Because ${}^3S$ of N II was obviously out of line with ${}^1P$ and ${}^1D$ of C I in the old classification, I suggested in part III that ${}^3S$ was due to some other configuration than sp^3; it is now evident that the old ${}^1D$, ${}^1P$ were the real culprits.) With the new classification and for more extensive data, the Johnson formulas fit experiment very much better than previously, in fact unusually well for *F-G* relations. The revised and extended version of Table I of part III is given in Table I.

TABLE I. *Energies, in volts, relative to the ground state* $s^2p^2\,{}^3P$.

	Observed			Calculated		
	C I	N II	O III	C I	N II	O III
$sp^3\,{}^5S$	[4.3]	5.8	7.4	(4.3	5.8	7.4)
$sp^3\,{}^3S$	13.0	19.2	24.4	(13.3	19.2	24.4)
$sp^3\,{}^3D$	7.9	11.4	14.8	8.2	11.8	15.2
$sp^3\,{}^1D$	[12.9]	17.8	23.1	12.6	18.5	23.7
$sp^3\,{}^3P$	9.3	13.5	17.6	(9.3	13.5	17.6)
$sp^3\,{}^1P$	[14.0]	20.6	26.0	13.7	20.2	26.1

The "observed" values in square brackets, unlike the others, are not really spectroscopic, but have been computed by Bacher and Goudsmit with their new extrapolation method. Their results are reliable to a few tenths of a volt, and better than the estimates 12.1 and 14.8 for ${}^1D$, ${}^1P$ which Edlén obtained with the irregular doublet law. The calculated values have been obtained by the Johnson formulas given in part III, with the parameters chosen so as to yield the proper positions for ${}^5S$, ${}^3S$, ${}^3P$. The corresponding magnitudes of the parameters are those labelled "empirical" in Table II; they would not be much altered if three other states were fitted instead of ${}^5S$, ${}^3S$, ${}^3P$. We make this selection for the three because it makes the maximum deviation between the calculated and observed values in Table I less than with most other choices and so represents a closer approximation to the method of least squares. The Bacher-Goudsmit procedure is sufficiently accurate that it is not important that one of the three states fitted has been located in C I by this procedure rather than spectroscopically.

The values in parentheses are those obtained in part III for carbon by fitting ${}^1P$, ${}^3D$, ${}^3P$ with the old classification. We have also listed for comparison the results of Beardsley's theoretical calculations by means of approximate wave functions obtained by a variational method. It is seen that the new classification largely removes the previous qualitative disagreement between the empirical values of the Johnson parameters and those computed by Beardsley.

With the empirical values of the parameters listed in Table II, one calculates from Eqs. (7) and (8) of part III

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[1] J. H. Van Vleck, J. Chem. Phys. **2**, 20 (1934).

[2] The following minor errata may be noted in part II (ibid. **1**, 219, 1933): add $\frac{3}{2}(1-\cot^2\theta)\sin^2\theta N_{xx}+\cot^2\theta N_{zz}$ to the expression (41); in the line before (41) read $\mathfrak{R}=0$ for $N=0$.

[3] B. Edlén, Zeits. f. Physik **84**, 746 (1933); I am indebted to Professor Bowen for calling my attention to this reference and to the use of the irregular doublet law in connection with it.

[4] Bacher and Goudsmit have as yet published only a preliminary abstract on their method; Phys. Rev. **45**, 559 (1934). They have, however, very kindly informed me of the results of the application to carbon in advance of their detailed paper.

TABLE II.

	Empirical			Beardsley
	C I	N II	O III	C I
G_1	2.18 (0.9)	3.35	4.25	3.44 volts
F_2	0.188(0.2)	0.290	0.400	0.29
W_0	13.7 (11.1)	20.2	26.1	14.6

that the energy of the "valence state" of carbon explained in section 2 of part III should range from 7.1 volts for the tetrahedral model $\mu=\frac{1}{4}$ to 8.5 volts for the model $\mu=1$ without hybridization. The effect of the L, S structure is thus not quite as trivial as we previously estimated, and favors the tetrahedral modal model slightly. Because of the successful application of Johnson's formulas to the new data, our estimate of 7 volts for the energy required to promote carbon to the tetravalent condition appropriate to CH_4 is now based on a much more certain calculation than formerly and is probably accurate to within half a volt. This estimate is fortuitously the same as that which we obtained in part III with the old values of the Johnson parameters. Hence sections 3 to 6 inclusive of part III, and so all the chemical applications in III, are mercifully unaltered.

J. H. VAN VLECK

Department of Physics,
University of Wisconsin,
Madison, Wisconsin,
March 21, 1934.

A Slight Difference in the Isotopic Composition of Oxygen Made by the Fractionation of Liquid Air and Oxygen of Ordinary Air[1]

In an investigation of the fractionation of the isotopes of hydrogen and oxygen by the electrolysis of water, a series of measurements has been made on the difference in density of ordinary water and of the water formed by: (1) combining the electrolytic hydrogen with commercial oxygen; (2) combining the electrolytic oxygen with commercial hydrogen; (3) recombining the electrolytic gases as they come from the cell. The commercial oxygen, made from liquid air, was assumed at the start to have the isotopic composition of ordinary oxygen as it exists in air and water. The commercial hydrogen, made electrolytically in cells which have been in operation for years, was shown to be normal by combining it with ordinary atmospheric oxygen and comparing the density of the water thus formed with that of ordinary water. The difference in density was only 0.3 part per million.

However, in every case the sum of (1) and (2) failed to check with (3) by amounts ranging from 1 to 3 ppm and always of the same sign. The discrepancy was finally traced to the assumption that the commercial oxygen was the same as the oxygen in normal air and water. This assumption was tested by preparing two samples of water, one composed of the dried commercial oxygen combined with dried hydrogen from a given cylinder, and the other composed of ordinary atmospheric oxygen and dried hydrogen from the same cylinder. After purification by distillations from alkaline permanganate and from phosphoric acid followed by simple distillation, with the rejection in each case of small first and last portions, the water from commercial oxygen was found to be heavier by 1.4 and 2.4 ppm. After an additional distillation the difference was 2.8 ppm, giving an average of 2.2 ± 0.5 ppm. Assuming adequate purification, this difference can result only from a difference in the two samples of oxygen.

The commercial oxygen was manufactured by the fractionation of liquid air in a column which produces nitrogen of 95.5 percent purity at the top, and apparently a slight fractionation of the oxygen isotopes occurs, so that the commercial oxygen has a density greater by about 2 ppm and therefore contains approximately 2 in 10^5 more atoms of O^{18}, than ordinary oxygen. This difference may vary somewhat with the efficiency of different fractionating columns and may be of significance in other investigations.

Before these measurements were completed Klar and Krauss[2] found differences in the isotopic composition of different fractions of technical oxygen. However, the results reported in this letter may be of some value since they confirm the results of Klar and Krauss and, in addition, show the magnitude of the change to be expected in the oxygen from an ordinary commercial cylinder.

EDGAR R. SMITH

Bureau of Standards,
Washington, D. C.,
March 27, 1934.

[1] Publication approved by the Director of the Bureau of Standards, U. S. Department of Commerce.

[2] R. Klar and A. Krauss, Naturwissenschaften **22**, 119 (1934).

The Magnetic Susceptibility of Ammonium Hexabromo-Hypoantimonate

At the suggestion of Professor Linus Pauling, I have determined the magnetic susceptibility of ammonium hexabromo-hypoantimonate, $(NH_4)_2SbBr_6$, in order to obtain some information about the valence of antimony in this compound.

The substance was prepared by the method of Ephraim and Weinberg.[1] It was dried by centrifuging. The product was a deep black powder, apparently similar to Ephraim's compound.

The determination of the specific magnetic susceptibility by the Gouy method led to a value, $\chi=-0.036\times10^{-6}$ cg, the substance thus being shown to be diamagnetic.

[1] Ephraim and Weinberg, Berichte **42**, 4450 (1909).

Ammonium hexabromo-hypoantimonate, therefore, does not contain unpolymerized complexes involving a quadrivalent antimony atom, for such complexes would contain an odd number of electrons and hence give rise to strong paramagnetism. It is probable that the substance is a double salt containing one trivalent and one quinquivalent antimony atom corresponding to the formula $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$. The observed diamagnetism could be made compatible with the presence of quadrivalent antimony by assuming that the quadrivalent antimony atoms occur in groups of two joined by shared electron-pair bonds, Sb : Sb, similar to the group Hg : Hg^{++} in mercurous salts. This, however, seems improbable because the stoichiometric formula, $(NH_4)_2SbBr_6$, suggests that each antimony atom is surrounded by six bromine atoms which would prevent close approach of the antimony atoms.

NORMAN ELLIOTT

Pasadena, California,
April 11, 1934.

The Infrared Spectrum of Methyl Deuteride

As a consequence of its high degree of geometric symmetry the methane molecule, with nine degrees of freedom of vibration, has only two active fundamental absorption bands, each triply degenerate. While the character of these bands justifies the tetrahedral model, they yield very little information regarding the dimensions and elastic constants of the system. The replacement of one of the hydrogens by an atom of deuterium introduces a preferred axis, with respect to which the molecule is symmetrical, and increases the number of active vibrations from two to six. Of these, three are single, introducing electric moments parallel to the axis, and three are double, giving rise to perpendicular bands.

We have observed all of these fundamental bands, and have determined the rotational structure of one of them, the lowest frequency parallel vibration. This consists of a strong and narrow zero branch at approximately 1090 cm^{-1}, and the usual positive and negative branches, the intervals between rotation lines being about 4.5 cm^{-1}. From this interval the maximum moment of inertia may be computed at once, $I \sim 12.28 \times 10^{-40}$, and the H-H distances are about 2.51×10^{-8} cm. More bands must be analyzed and the molecular constants evaluated before these dimensions can be given with precision. Assuming the atomic distances to be the same for ordinary methane, its moment of inertia comes out approximately 10.45×10^{-40}. As would be expected, this value is about twice as large as that determined from the rotational Raman effect by Dickinson, Dillon and Rasetti,[1] since they assumed that the successive lines have J values differing by two. They found $I = 5.17 \times 10^{-40}$.

Methyl deuteride is of especial interest in the study of rotational and vibrational interaction in perpendicular bands, since it is the first molecule available in which both moments of inertia may be determined precisely. Because the bands lie rather close together and overlap considerably, their analysis must await further study, and will be reported later.

A very interesting test of the assumption that the atomic distances are the same for both isotopes of hydrogen will be provided by the study of the methane molecule with three hydrogen atoms replaced by deuterium. These measurements we hope to publish within a short time, as well as the fundamental frequencies of tetra-deutero methane.

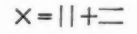
E. F. BARKER
NATHAN GINSBURG

University of Michigan,
April 13, 1934.

[1] Dickinson, Dillon and Rasetti, Phys. Rev. **34**, 582 (1929).

Resolution of Crossed Bond Eigenfunctions in Terms of the Uncrossed Set

The method of repeatedly applying the theorem for uncrossing any pair of bonds expressed by the relation



is adequate for resolving every bond eigenfunction in terms of the linearly independent set. However, the labor of doing this rises rapidly as the number of bonds increases. Since in obtaining bases for irreducible representations[1] the resolution of crossed bond eigenfunctions is practically unavoidable, some simplification seems necessary. Very simple rules have been found for the cases usually encountered, i.e., those involving 5 bonds or fewer.

We assume we have a crossed bond eigenfunction A with $2n$ orbitals arranged symmetrically on a circle connected in pairs by n bonds.

Rule I

The number of times this process of uncrossing will yield a particular bond eigenfunction B with no crossed bonds equals the number of different ways a set of n continuous, entirely noncoincident (except perhaps at points), noncrossing paths may be drawn along the lines in A, such that they connect each pair of orbitals bound together in B. Ordinarily this rule enables one to determine coefficients 0 or 1 by inspection, but in any case the determination is very simple. A subsidiary rule is necessary in cases yielding larger coefficients. Such cases arise when there is a point common to more than three paths.

[1] Eyring, Frost and Turkevich, J. Chem. Phys. **1**, 777 (1933).

Rule II

Draw the shortest set of n paths of the kind described in rule I. If there is a point common to p paths (only points for which p is 3 or greater are to be considered) the number of times B will occur in uncrossing A is $(p-2)$. In determining p we note that frequently for an eigenfunction A parts of the lines in A are not traversed by the set of n paths. All points connected by untraversed lines are for this purpose to be counted as one point. Having done this one further procedure may be necessary in applying rule II. Any path which passes through a point and which with the perimeter circle separates other paths common to the point into two groups is omitted in determining p for the point. This discarding is continued until there are no more such paths.

The coefficients for all uncrossed bonds are positive if the convention is adopted in every B and A of arranging the orbitals in order around a circle and always directing the arrow representing a bond toward the orbitals with the higher ordinal number.

These rules have been checked for all possible patterns of 5 bonds or less. A more complicated rule is required for direct application to more than 5 bonds. However, eigenfunctions involving 6 or more bonds are readily reduced by comparatively few uncrossings to cases to which our simple rules apply.

HENRY EYRING
CHENG E. SUN

Frick Chemical Laboratory,
Princeton University,
April 13, 1934.

On Diffusion Equilibria of Electrolytes

A study of the fundamental elements contained in the theory of electrolytic conductivity which will be reported later, has led among others, to some results about the limiting case, i.e., diffusion equilibrium under the influence of external forces.

Consider for the purpose of illustration the distribution of charged colloidal particles and ions in a gravitational field. If there are only very few ions present which carry charges of the same sign as those present on the colloidal particles, the problem can be solved with sufficient accuracy for dilute solutions. It is found that there occur large deviations from the Boltzmann distribution which tend to make the latter more uniform. At the same time the rate of establishment of equilibrium is greatly reduced. An increase in concentration tends to diminish the deviation from the Boltzmann distribution. The presence of ions carrying charges of the same sign as the colloidal particles acts in the same direction.

Similarly it can be shown that the diffusion potential in electrolytes does not assume its classical value.

These effects can perhaps be described by the statement that the activity coefficients of the charged particles lead to an apparent reduction in the value of their diffusion coefficient.

The writer hopes to be able to present shortly a more detailed account of these investigations.

OTTO HALPERN

New York University,
University Heights,
April 14, 1934.

Observations on the Synthesis of Tetra-Deutero Methane

In the course of the synthesis of tetra-deutero methane with the object of studying its physical properties, we have made some observations on the relative velocities of reactions between the proto water and aluminum carbide and the deutero water and aluminum carbide.

Carefully prepared aluminum carbide in fairly finely divided form was placed in a sealed container fitted with a small reflux condenser, and the proto water added at low temperatures. The whole system was evacuated and the mixture allowed to come to room temperature. Gas bubbles formed at ordinary temperatures and in the course of 10 or 15 minutes raised the pressure in the apparatus to atmospheric. The mixture was then raised to about 80°C and the methane generated collected over mercury. It required on the average 2 minutes to collect 100 cc of methane.

With the same apparatus and aluminum carbide from the same batch and of the same fineness of division, the same method was attempted using the deutero water. At room temperatures, no reaction took place in the course of two hours. We then filled the apparatus with CO_2 at atmospheric pressure and raised the temperature to 80°. It now required 46.5 minutes to collect the first 100 cc of methane gas. This gives a ratio of the velocities for the two reactions of approximately 23. This seems to be the highest ratio so far observed for reactions involving compounds of the two hydrogens. Not until the reaction vessel was heated to about 65° were we able to see any bubbles of methane form in the reaction vessel. The next 100 cc were collected at 90°. At this temperature, the rate of evolution of the gas was about three times that at 80°.

The temperatures were controlled by maintaining the temperature of a water bath within a degree or two of the temperatures given. There is a possibility, of course, of slight error in this way, but that there is an enormous difference in the velocities of the reactions cannot be doubted.

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The Diffusion of Hydrogen Through Metals: Fractionating the Hydrogen Isotopes

Dr. L. B. Tuckerman of the Bureau of Standards, referring to our note appearing on page 105, February, 1934, *Journal of Chemical Physics*, has called our attention to the fact that diffusion of nascent hydrogen through metals is nothing new. We certainly did not want to give that impression. We only observed what to us was a striking example of a well-known phenomenon. Particularly noteworthy are the researches of Sainte-Claire Deville (Comptes Rendus **59**, 102 (1864)), Cailletet (Comptes Rendus **66**, 847 (1868)), and Graham (Proc. Roy. Soc. **A16**, 422 (1868)), and the later work by Bellati and Lusana (Atti. Instit. Veneto (7) **1**, 1173 (1890); **2**, 987 (1891)). The work of Cailletet is especially interesting. He allowed electrolytic hydrogen to pass through an iron tube and developed pressures of the order of 20 atmospheres.

Our note was specifically directed to the possibility of separating the hydrogen isotopes by means of selective diffusion of these through metals at room temperature. "We decided to determine whether or not the hydrogen thus collected within the metal pillow was substantially the lighter of the two hydrogen isotopes." If we have given our readers the impression that we thought that the diffusion of electrolytic hydrogen through metals was new, we are glad to take this opportunity to correct any such impression.

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